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# Lewis Acids as Catalysts in Oxidation Reactions: From Homogeneous to Heterogeneous Systems

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## I. Introduction and Scope

This review is focused on the use of solid Lewis acids to promote catalytic oxidations. While the concept of using Lewis acids to promote the reaction of organic substrates with oxidizing reagents is widely accepted in homogeneous catalysis, this concept has not become evident and generally used in heterogeneous catalysis until recent days. Certainly the development of new Lewis acid solids active and selective for catalytic oxidations is an urgent need and a challenging scientific target for some substrates especially using environmentally friendly oxidants. Since the replacement of current stoichiometric oxidations for the production of fine chemicals by environmentally benign catalytic oxidations is one of the major tasks in green chemistry, solid Lewis acids are called to play a crucial role to accomplish this goal.

In the review, we will see the still important role that stoichiometric oxidations play in our daily life, and how they are being substituted by catalytic oxidations. At this point, three general mechanisms in which Lewis acids are involved will be described, and the material has been organized starting from homogeneous and ending with solid catalysts for heterogeneous oxidations. A bridge between the two will be established by presenting catalytic systems that can fill the gap between the two systems helping to rationalize the nature of the catalytic active sites in solid systems.

This review is obviously focused on solid oxidation catalysts, and the core of the review is organized to show the evolution from the simplest strategy for heterogeneizing homogeneous catalysts, i.e., supporting the active species on large surface area solids, to the more elaborate ones in which the active sites are part of the solid structure. Given the importance of metallosilicates, and more specifically titanosilicates, as catalysts in commercial processes, special attention has been paid to these types of materials.

Although sufficient references are provided to early seminal work, special emphasis has been given to most recent contributions to this area, particularly of the last 10 years. Patent literature has also been extensively covered in this review. Examples to illustrate the concepts have been selected among recent publications, and an effort has been made to present a series of commercial and near commercial processes based on catalytic oxidations. Finally, two

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Avelino Corma Canos was born in Moncófar, Spain, in 1951. He studied chemistry at the Universidad Complutense de Madrid in 1976. He is director of the Instituto de Tecnología Química (UPV–CSIC) at the Universidad Politécnica de Valencia since 1990. His current research field is zeolites as catalysts, covering aspects of synthesis, characterization, and reactivity in acid–base and redox catalysis. Avelino Corma has written about 500 articles on these subjects in international journals, three books, and a number of reviews and book chapters. He is coauthor more than 45 patents, six of them being commercialized. He is a member of the Editorial Board of 10 international journals in the area of chemistry. He has been awarded the Dupont Award on new materials (1995), the Spanish National Award "Leonardo Torres Quevedo" on Technology Research (1995), Burdiñola (1997), Premio Iberdrola de Química, (1998) and F. Ciapetta Award of the North American Catalyst Society (1998), Ipatieff Lecturer at Nortwestern University 2000/01, "Rey Jaime I" Award on New Technologies (2000), François Gault Lectureship (EFCATS) (2002).

Hermenegildo García (Herme) was born in Canals (Spain) in June of 1957 and studied chemistry at the Faculty of Science of the Universidad de Valencia (Spain) where he graduated in 1979 with Honors. He did his Ph.D. on preparative organic photochemistry under the guidance of Prof. Miguel A. Miranda and was awarded also with Honors by the Universidad de Valencia in 1983. Then, he moved to the Technical University of Valencia where he initiated his career in 1983 first as Assistant Professor, becoming finally Full Professor in 1996. In 1991, he was appointed member of the Institute of Chemical Technology, a join center depending on the Spanish National Research Council (CSIC) and the Technical University of Valencia that was founded at that time. He did a postdoctoral stay at the Chemistry Department of the University of Reading (U.K.) with Prof. Andrew Gilbert in 1987, and later three successive sabbatical leaves in 1992–1993 (one year), 1995 (six months), and 2000 (three months) at the University of Ottawa joining the Laser Flash Photolysis group leaded by Prof. J. C. (Tito) Scaiano. He has coauthored over 200 papers most of them dealing with the application of zeolites as hosts of organic guests and as solid catalysts. He holds three international patents. His main current interests are in supramolecular photochemistry and photocatalysis, development of photoactive nanoscopic materials, and heterogeneous catalysis.

short sections have been devoted to present how catalytic oxidations can be used to eliminate a series of pollutants, and how catalytic oxidations are present in our domestic life.

## II. Oxidation Strategies

Since the beginning of the petrochemical industry, oxygen was the only possible oxidant that could be used in the production of bulk chemicals due to the huge production volumes and the economics of the processes. The higher added value of specialty chemicals allows the choice among other oxygen atom donors such as $H_2O_2$, alkyl hydroperoxides, and sodium hypochlorite.

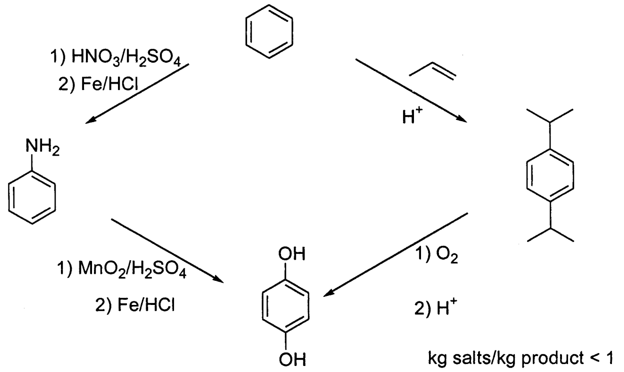
Fine chemicals and pharmaceuticals are characterized by a much lower production volume and much higher added value. In addition, from the chemical point of view they encompass a wide diversity of chemical structures, often relatively complex and having concurrently different functional groups. This complicates enormously the transfer of a chemical process from the synthesis of a given fine chemical to a different one. In practice, the synthesis of each individual chemical is considered independently and surely requires a specific research and development to be implemented. Also, their high molecular weight and the presence of functional groups generally precludes performing oxidations in the gas phase and the processes for the production of fine chemicals have to be necessarily developed in the liquid phase, very frequently in a multipurpose batch reactor.

In the synthesis of fine chemicals, the chemo-, regio-, and stereoselectivity of the oxidation reaction is the crucial issue. The wide diversity in structures, combined with the relatively low production volume and the need of selectivity, explains why innovation in these industrial oxidations did not become a priority.

Noncatalytic, stoichiometric oxidation using conventional oxidants are still in use for numerous processes involving the oxidative C═C double bond cleavage, the transformation of primary and secondary alcohols into acid derivatives, aldehydes and ketones, heteroatom oxidation, oxidation at allylic and benzylic positions, etc. Stoichiometric oxidants are used in the production of a very wide number of pharmaceuticals, fragrances, agrochemicals, etc.; traditional oxidation methods involve the use of stoichiometric quantities of high oxidation state Cr, Mn, or Os reagents, among others.[1]

Despite the important role still played by stoichiometric oxidations, the general trend is the development of catalytic processes to replace traditional stoichiometric oxidants such as dichromate, chromate, permanganate, manganese dioxide, osmium tetroxide, lead tetraacetate, etc. The need to develop alternative environmentally friendly catalytic oxidations derives not only from the nature and potential toxicity of the metal present in the stoichiometric oxidant, but also from the general principle of green chemistry to reduce the volume of byproducts formed in the overall synthetic route. In catalytic oxidations, the stoichiometric oxidants are molecular oxygen, hydrogen peroxide, alkyl hydroperoxide, persulfate, percarbonate, perborate, hypochlorite, etc., that do not release any metal ion as a byproduct in the process.

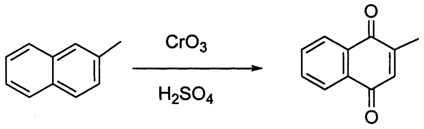
**Scheme 1**



Two related examples in which an obsolete way to produce a chemical using a stoichiometric oxidant has been replaced by a catalytic oxidation are the preparation of hydroquinone from benzene and the production of 2-methyl-1,4-naphthoquinone (menadione) that is an intermediate for vitamin K. In the first case (Scheme 1), not only the number of steps has been reduced and the stoichiometric oxidant replaced, but also the ratio between the weight of byproducts to the final product in the overall synthesis was decreased from over 10 to less than one.[2,3]

In the production of menadione (Scheme 2), the conventional route using chromium trioxide in sulfuric acid formed 18 kg of inorganic salts. This process was substituted by catalytic oxidation using 60% aqueous hydrogen peroxide over palladium(II) exchanged polystyrenesulfonic acid resin.[4]

**Scheme 2**



The fact that Lewis acid sites can catalyze oxidation reactions is not sufficiently recognized and exploited in heterogeneous catalysis. Very frequently, solids containing transition metals are termed as redox catalysts, but they act in reality as solid Lewis acids. It is well established that soluble Lewis acids can act as promoters of oxidation reactions, and sufficient examples of this will be provided in the corresponding section.

Three are the general ways in which a Lewis acid can catalyze oxidation reactions:

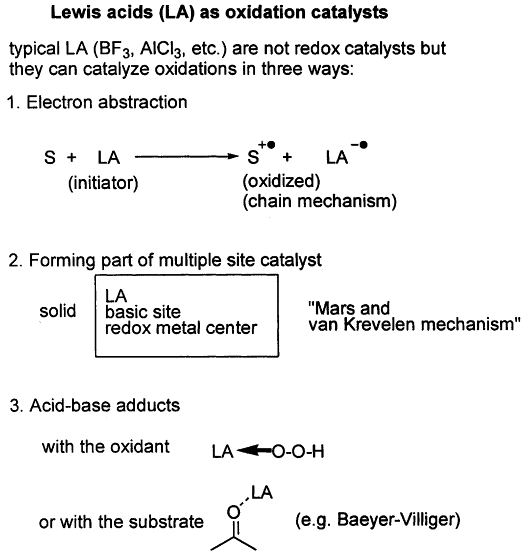
(i) A Lewis acid can abstract a single electron from an electron-rich molecule.

(ii) The oxidation catalytic center is an assembly of a Lewis acid site, a Lewis basic site, and a metal atom that undergoes variation in its oxidation state through the catalytic cycle.

(iii) A Lewis acid can catalyze oxidation reactions by forming acid−base adducts either with the substrate or with the oxidizing agent, enhancing their reactivity and thereby acting as catalyst for the oxidation.

The review has been organized by addressing each of these Lewis acid-catalyzed oxidation mechanisms in separate sections showing in each case the transition from homogeneous to heterogeneous catalysis.

**Scheme 3**

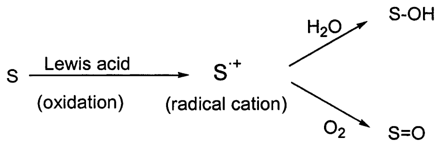


## III. Lewis Acids as Oxidation Catalysts

## A. Oxidations by Single Electron Abstraction

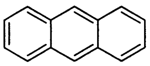
Single electron transfer is in essence the most elementary oxidation in which oxidation is defined as a process in which a substrate losses electrons. Although electron abstraction by conventional Lewis acids is well documented, the location of the electron accepted by the Lewis acid cannot be frequently determined. The resulting organic radical cation is a highly reactive, short-lived reaction intermediate that can be subsequently trapped by water or any other nucleophile present in the medium or by oxygen,[5−7] and at the end oxygenated products are formed (Scheme 4). We will summarize briefly this type of process below.

**Scheme 4**

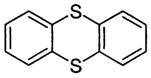


Benzene associates with strong Lewis acids such as antimmony pentafluoride or boron trifluoride in sulfur dioxide as a solvent.[8] The oxidation potential of benzene is lowered by this interaction, and the stronger the association with the Lewis acid the largest is the reduction of the potential. Values of 1.6 and 1.1 V have been determined for $BF_3$ and $SbF_6$, respectively.[8] This decrease in the oxidation potential is responsible for benzene polymerization to form poly(*p*-phenylene) polymer.

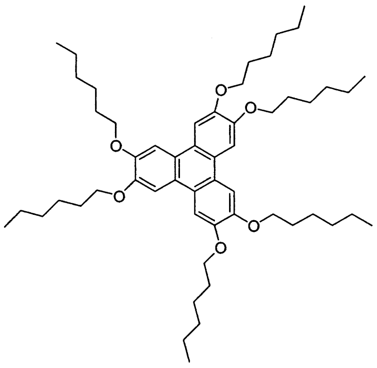
$AlCl_3$-doping can also serve to generate organic radical cations through electron abstraction from electron-rich substrates. Electron-rich aromatic and heteroaromatic compounds such as anthracene and thianthrene are readily converted into their corresponding radical cations by adding anhydrous $AlCl_3$ in a polar, inert solvent such as liquid $SO_2$.[7] Analogously, quasi-monodimensional p-type semiconductors can be obtained by adding small amounts of $AlCl_3$ into the hydrocarbon chain matrix of discotic liquid crystals such as those derived from hexahexyloxytriphenylene.[9,10]



anthracene

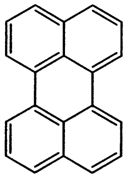


thianthrene



Hexahexyloxytriphenylene

Lewis acid sites have been proposed to be responsible for the aerobic oxidation of polycyclic aromatic compounds adsorbed on silica and zeolites. For instance, tetracene gives rise to 5,12-tetracenequinone as the major product together with lesser amounts of 5,12-dihydroxytetracene and 5,12-dihydro-5,12-dihydroxytetracene following a first-order rate constant of $1 \times 10^{-5}$ $s^{-1}$.[11] Apparently, the reaction intermediates involved in this process are the corresponding radical cations of the electron rich aromatic generated through electron transfer from the arene to the Lewis acid sites.

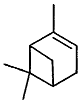


Tetracene

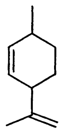
Given the simplicity of the electron transfer generation of aromatic radical cations and their ability to react with molecular oxygen to form oxygenated products with high selectivity, it is surprising that these reactions have not yet been exploited in large-scale industrial processes. They will require only to have sufficiently high oxidation potential Lewis acid sites to generate the radical cation intermediate.

A practical scale for measuring the ability of the acid sites of a solid for the generation of radical cations versus truly acid behavior has been proposed based on the combination of reactant test molecules and quantification of the radical cation population by means of EPR spectroscopy.[12] 1,4,5,8-Tetramethylnaphthalene undergoes a facile acid (either Brönsted or Lewis) rearrangement to 1,3,5,8-tetramethylnaphthalene and then to other tetramethylnaphthalene isomers. In contrast, the corresponding radical cation of 1,4,5,8-tetramethylnaphthalene is stable and does not undergo any rearrangement.[12] By measuring the extent of methyl rearrangement and radical cation population, a scale of the capability of acid sites toward electron-transfer abstraction can be obtained for a series of oxidant-solvent combinations. This test reaction appears to be very useful to quantify acidity versus oxidation ability of Lewis acids and their applicability deserves to be demonstrated in other systems.

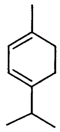
Lewis acids of zeolites are also known to generate organic radical cations. By combining an EPR study of the generated radical cations with MAS $^{27}Al$ NMR spectra of dealuminated mordenite, a relationship between the presence of Lewis acid sites and the oxidizing ability of mordenite has been proposed.[13] Thus, the radical cation of 2,5-dimethyl-2,4-hexadiene is characterized by EPR after adsorption of 2,5-dimethyl-1,5-hexadiene or 2,5-dimethyl-3-hexene on dealuminated mordenite. The intensity of the signal correlates with the presence of extraframework Al. When extraframework Al is removed by mineral acid leaching or chelation with oxalic acid, only a very weak EPR signal was detected. Thus, it was proposed that although Brönsted acid sites may be responsible for the major catalytic activity of mordenite, its ability to abstract one electron to generate persistent radical cations relies on extraframework Al.[13] Analogously, incorporation of α-pinene, *trans*-isolimonene, and α-terpinene in H-mordenite allows one to record the same EPR spectrum that was assigned to α-terpinene radical cation.[14] From the lack of deuterium labeling when α-pinene was adsorbed on deuterated mordenite, it was concluded that the rearrangement to α-terpinene is not catalyzed by Brönsted acid sites, but most likely by Lewis acids which would be responsible for the single electron oxidation of the three terpenes.[14]



α-pinene



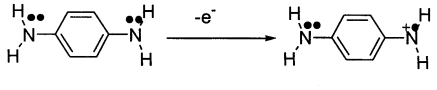
*t*-isolimonene



α-terpinene

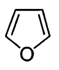
Vanadium(IV) and oxovanadium(IV) Schiff base complexes have been prepared and were found to exhibit catalytic activity toward the aerobic oxidation of *p*-phenylendiamine to the corresponding semi-oxidized radical cation form (Scheme 5).[15]

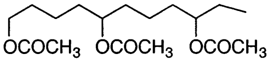
**Scheme 5**



On the other hand, oxovanadium complex catalyzed oxygenation of disulfides is likewise facilitated by Lewis acids. It has been found that the activation of Lewis acids for the electron transfer to quinones and oxygenation with oxovanadium have in common a decrease in the oxidation potential of the diaryl disulfides, thus, facilitating their single electron oxidation.[16] It was found that catalytic amounts of Lewis acid (substrate/Lewis acid ratio 200) promotes polymerization of diaryl disulfides through a mechanism that involves the electron transfer from the diaryl disulfide to an equivalent amount of an oxidizing reagent such as *p*-benzoquinone.[16] Compared to Brönsted acids such as trifluoracetic acid, $SbCl_5$ and $FeCl_3$ are over 200-fold more active to facilitate the electron transfer between diphenyl disulfide and *p*-benzoquinone in which linear poly(thio-1,4-phenylene) is formed.

Transition metal oxidative polymerization followed by concomitant doping of the resulting conjugated oligomer or polymer is sufficiently documented in the literature.[17,18] Doping of conjugated polymers increases enormously their electrical conductivity and is necessary in many of the potential applications of these materials. A procedure to obtain oligofurans with a high degree of conjugation and with an ordered aromatic structure consists of treating furan with $FeCl_3$ as the oxidizing reagent in polar aprotic solvents, such as propionitrile.[19] The resulting oligomer is soluble in organic solvents and when blended with poly(ethylene-*co*-vinyl acetate) a film with good mechanical resistance can be cast. The electrical conductivity of these films containing well-polymerized polyfuran after $I_2$ doping is several orders of magnitude higher than that reported earlier for intractable polyfurans.[19]

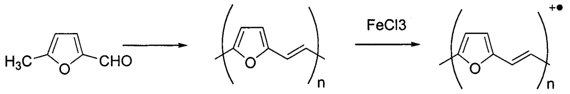

furan



poly(ethylene-co-vinyl acetate)

Poly(2,5-furandiylvinylene) can be prepared by aldolic condensation of 5-methylfuran-2-carbaldehyde in a single step (Scheme 6).[20] This polyfurandiylvinylene can be doped with Lewis acids such as $AsF_5$ and $FeCl_3$ or iodine. The electric conductivity varies from $10^{-8}$ S cm$^{-1}$ for the polyfuran to $10^{-2}$ S cm$^{-1}$ for the $AsF_5$ doped material.[20]

**Scheme 6**



Transition metals have been used to effect the chemical[21,22] or electrochemical polymerization[23] of pyrrole in water. $FeCl_3$ is a general reagent to effect the polymerization of conducting polymers from five-member ring heterocycle monomers.[24] Polyaniline exhibiting a low polydispersity and high solubility in organic solvents can be obtained by oxidative polymerization with $H_2O_2$ using transition metal as catalysts.[25]

Lewis acids such as metal chlorides oxidize the $\pi$ electrons of conjugated polyene sequences formed in the dehydrochlorination of PVCs.[26] As result of this electron transfer, polarons of the incipient conjugated polymer are formed, which accelerate the chain mechanism of the dehydrochlorination. In contrast, organotin chlorides intercept the alkyl chains and produce the retardation of PVC dehydrochlorination.[26] These processes are related to the degradation of PVC and the way in which it can be protected, and they have a considerable economic impact given the ample use of PVC.

The previous examples demonstrate that, in contrast to the general belief, Lewis acids can truly act as oxidation catalysts when the organic substrate has a sufficiently low oxidation potential and the corresponding radical cation is generated. In other cases, however, the reaction mechanism is more complex and the Lewis acid sites alone do not promote oxidation but they cooperate with other sites present in the catalyst. A classical example of this is the Mars and van Krevelen oxidation mechanism discussed in the next section.

## B. Oxidations by an Assembly of Lewis Acid, Lewis Basic, and Redox Centers

In these type of oxidations, the catalytic center is in reality an assembly of a Lewis acid site, a Lewis basic site, and a metal atom that undergoes variation in its oxidation state through the catalytic cycle. This type of catalytic mechanism follows what is known as a “Mars and van Krevelen” mechanism.[27−34]

The structure at the atomic level of active sites of metallic oxides that catalyze oxidation reactions via Mars and van Krevelen mechanism has been recently reviewed.[32] The structure, size, and relative strength of each of these individual sites, that conform the catalytic centers, are termed as “inorganic oxide molecular clusters” and define the overall activity and specifity of the bulk solid catalyst. The Mars and van Krevelen mechanism is one of the most general mechanisms for oxidation reaction in metallic oxides, being the cooperation of acid−base and redox sites the key point for catalysis.[31] It consists of a series of elementary steps that include: (i) activation of the substrate on a metallic cation; (ii) insertion of oxygen from lattice oxygens; and (iii) a redox process at the metallic site and the transfer of one or several electrons. In the first step, metallic cations act as Lewis acid sites, and the basic sites are surface $O^{=}$ or $OH^{-}$ species. The substrate undergoes hydrogen abstraction, oxygen insertion, and electron transfer. Thus, the active sites require a spatial organization at atomic level and the cooperation of distinctive atoms.[31] Some examples of processes that are believed to occur through this mechanism include the oxidation of butane to maleic anhydride, isobutyric acid oxidative dehydrogenation to methacrylic acid on hydroxy phosphates, and propane oxidative dehydrogenation to propene on magnesia-supported vanadium oxide. In the latter case, it is known that the overall activity of the catalysts depends on the basicity of the support and on the presence of isolated $VO_x$ sites. Water has been found to be necessary in some cases to provide hydroxylated surface sites allowing the reaction mechanism to operate.[31]

Several transition metal oxides and ions are active catalysts for the selective oxidation of hydrocarbons, and the catalytic activity can also be explained based on their acid−base properties. In this way, higher valent incompletely coordinated metal ions or anionic vacancies on oxide surfaces can act as acidic sites, and oxygen ions, $O^{2-}$, as basic sites. The influence of the acid−base properties on the selectivity for hydrocarbon oxidations has been largely reported in the literature.[35−38]

### 1. Vanadium-Based Systems

Vanadium is among the most active transition metals capable to effect alkane oxydehydrogenation, oxygenations, and alkylaromatic oxidations. In this regard, vanadium phosphates and aluminophosphates, as well as supported vanadium oxides, are widely used for this purpose. In the next two sections, we will comment on the catalytic activities of these vanadium-containing solids and the established relationship with Lewis acid sites.

**a. Influence of the Acidity on the Catalytic Activity of Vanadium Phosphate.** In agreement with the Mars and van Krevelen mechanism, surface characterization techniques have provided some evidence in support of the presence of Lewis acid and basic sites during the operation of vanadyl phosphates as oxidation catalysts. Thus, high-resolution and in situ electron microscopy of vanadyl pyrophosphate after being reacted with *n*-butane or other reducing molecules has shown that the surface structure undergoes a significant modification during the catalytic process.[39] Two sets of symmetry related defects are created during the catalytic reaction. It is suggested that these defects are oxygen vacancies at sites linking corner-sharing phosphorus tetrahedra and vanadyl octahedra in the active plane.[39] These vacancies create Lewis acid centers. It is proposed that these defect sites play a key role in the activation of the alkane, particularly for selective dehydrogenation reactions.[39] Accordingly, this interpretation would indicate that oxygen atoms of the catalyst are consumed during the reaction.

For the selective oxidation of *n*-butane to maleic anhydride by vanadyl pyrophosphate, the process is supposed to occur specifically on the (1.0.0) face of crystal. This assumption is supported by the spatial distribution of the atoms in the catalyst exposed to the C−C and C−H bonds of *n*-butane.[40]

Vanadium phosphate catalysts have been modified by developing the (2.2.0) plane of $VOHPO_4{\cdot}0.5H_2O$ and introducing bismuth in its composition. The change in the surface characteristics by varying the P/V ratio results in an increase in the number of Lewis acid sites and the ionic strength of such sites, leading to an enhanced catalytic activity for the oxidative dehydrogenation of ethane and an increased yield of ethylene.[41] Also ferric phosphate with and without Pd impregnation is active for the oxidative dehydrogenation of isobutyric acid to methacrylic acid. During this reaction, amorphous $FePO_4$ undergoes reduction to $Fe_2P_2O_7$ at ~300 °C. The presence of palladium metal facilitates this reduction.[42]

In some cases, acidity may play a negative role, as is the case for the selective catalytic oxidation of para-substituted toluenes to the corresponding benzaldehydes over vanadyl pyrophosphate.[43] Benzaldehyde adsorption on the catalyst surface largely facilitates deeper oxidation to aromatic carboxylic acids. Coadsorption of pyridine suppresses the strong aldehyde adsorption and improves benzaldehyde selectivity. Electron donating para-substituents favor the aldehyde adsorption on the catalyst and cause their total oxidation.[43]

Vanadium phosphate supported on $TiO_2$ has been tested for the oxidative dehydrogenation of propane at temperatures between 300 and 400 °C, showing satisfactory performances (80% selectivity to propene at 2% propane conversion at 300 °C, and 56% propene selectivity at 9% propane conversion at 400 °C). Addition of water or pyridine to the feed decreases propane conversion but increases propene selectivity.[44]

Vanadium phosphate and other vanadia-supported solids are also catalysts for the oxidation of butane to maleic anhydride. It is under discussion whether this reaction requires the presence of one or more vanadium sites. By means of in situ Raman spectroscopy, it has been proposed that the selective oxidation of *n*-butane to maleic anhydride is more efficient at sites with more than one vanadium atom.[45] A recent mechanistic investigation of *n*-butane oxidation using $^{13}C$-labeled butane has been interpreted, however, assuming that the two methyl groups bind to a single vanadium atom through a cyclic organometallic intermediate.[46] An industrial process for the butane oxidation to maleic anhydride (Alusuisse Italia-Lummus Crest maleic anhydride or ALMA) based on the use of unsupported $(VO)_2P_2O_7$ in a fluidized bed reactor has been reported.[47]

In situ Raman spectroscopy as well as low-temperature CO adsorption monitored by IR suggests that the reversible oxidation and reduction between vanadyl pyrophosphate and a phase of vanadyl phosphate operates on the surface during the selective oxidation of *n*-butane exhibiting a relatively high selectivity toward maleic anhydride.[48]

In general, the influence of metal dopants and promoters on vanadium phosphates are discussed in terms of the Lewis acidity that they introduce in the solid. Thus, the influence of a series of promoters (Nb, Si, Ti, V, Zr, Cr) for the *n*-butane oxidation to maleic anhydride over bulk vanadium phosphorus oxide has been compared with that occurring on supported vanadia.[49−51] It was concluded that in both cases the catalysts requires the simultaneous presence of surface redox and acid sites and that the acidity also plays a role controlling further kinetic steps of *n*-butane oxidation. In this way, a correlation between maleic anhydride selectivity and the Lewis acidity of the promoter cations and oxide support in the case of supported vanadia has been found.[50]

It has been found that niobium phosphate acts as promoter for the vanadyl pyrophosphate oxidation of butane to maleic anhydride.[52] Apparently, $(NbO)PO_4$ is isostructural to $\alpha$-$(VO)PO_4$ both having a tetragonal structure, while the resulting mixed phosphate maintains the oxidizing capability of $(VO)_2P_2O_7$ together with a strong Lewis acidity introduced by Nb.[52]

Characterization of the surface acidity of vanadium−phosphorus oxide catalysts with XRD pattern of vanadyl pyrophosphate has been undertaken using ammonia, pyridine, and acetonitrile as basic probes monitoring by IR spectroscopy.[53] The stronger bases detected the presence of both Brönsted and Lewis acid sites, whose ratio increased with the temperature indicating that Brönsted centers are stronger than the Lewis sites. A study of the use of these mixed oxides as catalysts for the oxidation of *n*-butane to maleic anhydride revealed that the yield of anhydride and the proportion of the strongest Lewis acid sites increases with time on stream, thus suggesting a relationship between both.[53]

In another study, the adsorption of ammonia on the surface of vanadyl pyrophosphate[54] used as catalyst for the ammoxidation of propane to acrylonitrile has been monitored by IR spectroscopy. Ammonia is adsorbed on Brönsted and Lewis acids sites. At room temperature, ammonia forms mainly ammonium, but increasing the temperature up to 400 °C results in a progressive increase in the proportion of ammonia coordinated to surface Lewis sites.[54] The presence of gaseous oxygen lowers the amount of coordinated ammonia, probably due to the formation of amido “$NH_2$” species. Propylene is adsorbed as a $\pi$-complex to the vanadium Lewis acid sites and in the absence of oxygen is transformed into acrylonitrile through the intermediacy of propylamine. On the other hand, propane does not form detectable adsorbates in the absence of oxygen, but in its presence the formation of acrylate is observed.[54] This observation has led to the conclusion that two alternative pathways of acrylonitrile formation from propane operate in vanadyl pyrophosphate. The first in anaerobic conditions goes through propylamine, and the second, when oxygen is present, involves the reaction of acrylate and chemisorbed ammonia species, the latter pathway being much more rapid than the first.

**b. Influence of the Acidity on the Catalytic Activity of Supported Vanadium Oxides.** Supported vanadium oxides are among the most important heterogeneous catalysts for the vapor-phase oxidation of alkylaromatics, alcohols, and alkenes.[55−58] It is well-known in this type of catalysts that the nature of the metal oxide support plays an important role modulating the nature of V species and the catalytic behavior for oxidation reactions. Vanadium dispersion (related to the loading and the nature of the support) and acidity of the catalyst are the main factors to be considered.[59−61] A correlation between the isoelectric point (acid−base character) of the support and the photoluminescence of V=O groups has been recently found.[62] Acidity also plays a crucial role in the catalytic activity of the supported vanadium oxide.[63]

Kinetics and mechanistic studies of the oxidative dehydrogenation of propane over a series of vanadium, molybdenum, and tungsten oxides supported on zirconia have led to the suggestion that the rate determining step is the C−H bond activation using lattice O atoms (basic sites).[64] The activation energy of this step depends on the identity of the cation and increases in the order $VO_x/ZrO_2 < MoO_x/ZrO_2 < WO_x/ZrO_2$. Propane oxidative dehydrogenation activation energies are higher than those for propene combustion, but the relative rates of these reactions most probably also depends on the adsorption enthalpies for propene and propane. The latter parameter is mainly influenced by the Lewis acidity of the cations through $\pi$ bonding with the C=C double bond. This explains the observed difference in activation energy between propane oxidative dehydrogenation and propene combustion, that increases as the Lewis acidity of the cations increases ($V^{5+} < Mo^{6+} < W^{6+}$).[64]

Potassium doping has a beneficial influence on the selectivity of alumina-supported vanadium oxide catalysts for the oxydehydrogenation of butanes.[65] Apparently, addition of potassium results in a higher dispersion of vanadium species on the alumina support. This together with the presence of small amounts of $K_2O$ clusters leads to a decrease in the amount of exposed $Al^{3+}$ Lewis acid sites and a lower redox ability of vanadium species.[65]

For all the supported vanadium oxide catalysts, the vanadium loading is a parameter of paramount importance in the catalytic activity of the solid. As the vanadium loading increases, aggregation occurs, thus, varying the nature of the vanadium species and their catalytic properties. For instance, for the catalytic behavior of $\delta$-alumina-supported vanadium oxide for the oxidative dehydrogenation of ethane and *n*-butane, it has been observed that the activity for dehydrogenation increases as the vanadium loading, while the selectivity toward alkene formation reaches a maximum at 3−4 wt %.[66] Apparently, the highest propene yields require of a solid containing redox sites of adequate potential combined with strong Lewis acid sites and mild basic sites.[66] These findings seem to be in agreement with the operation of a Mars and van Krevelen mechanism, that requires the combination of these three type of sites.

Likewise, the selectivity of a series of catalysts based on vanadia supported on metal oxides toward the oxidation of *n*-butane to maleic anhydride as a function of the loading shows that while the overall turnover number for butane oxidation is independent of the surface coverage of vanadium oxide, the selectivity toward maleic anhydride increases by a factor of 2−3 as the vanadium oxide coverage increases approaching monolayer coverage.[67] These observations were interpreted as indicating that *n*-butane oxidation only requires a single site, while formation of maleic anhydride requires the cooperation of a pair of vanadium sites. On the other hand, the metal oxide support influences both *n*-butane oxidation and maleic selectivity in a different way. It was found a correlation between the Lewis acid strength of the oxide support and the maleic anhydride selectivity.[67]

Divanadium pentoxide has been dispersed on a series of oxide supports including $SiO_2$, $TiO_2$, $SnO_2$, $TiO_2/SiO_2$, $MoO_3/SiO_2$, and $SnO_2/SiO_2$ and the activity of the resulting solids as catalysts studied for the partial oxidation of methane to formaldehyde.[68] The activity of these catalysts was also a function of the surface coverage. At very low conversions, formaldehyde selectivity increases linearly with the surface coverage, indicating that isolated V(V) species are responsible for the catalytic effect. In the case of $V_2O_5$ supported on $SiO_2$, the selectivity reaches a maximum at 1%, and the decrease in the selectivity at higher coverages was explained as derived from an increase in the Lewis acid strength of the solid.[40]

The catalytic activity of vanadium oxide can be promoted by Lewis acid assistance of the support as, for instance, in alkane oxidation. Thus, studies of the structure and reactivity of group V metal oxides have been carried out by means of methanol adsorption and oxidation.[69] It has been found that the active sites present in pure $V_2O_5$ are primarily redox sites and the active sites in pure $Nb_2O_5$ are essentially acidic in nature. Furthermore, the surface redox sites present in pure $V_2O_5$ are orders of magnitude more active than the surface acid sites in pure $Nb_2O_5$ and consequently the catalytic activity of $V_2O_5/Nb_2O_5$ mixed oxides is largely dominated by the vanadia component.[69] However, niobia presence enhances significantly the activity of vanadia for those catalytic reactions that require a dual nature of redox and acid sites. This is the case of butane oxidation to maleic anhydride and the selective oxidation of ammonia by $NO_x$.

In some cases such as magnesium meta-, ortho-, and pyrovanadates, the relative low activity toward alkane oxydehydrogenation as compared to other vanadia-supported selective oxidation catalysts such as $V_2O_5/TiO_2$ and $(VO)_2P_2O_7$ has been attributed to the basic environment generated by the MgO support, which causes a parallel decrease of the Lewis acidity influencing the oxidizing power of the active V ions.[70]

On the contrary, the activity of $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_x$ supported on $\delta$-alumina, titania, silica, niobia, and zirconia for the direct conversion of propane to acrolein has been found to increase as the amount of Lewis acid sites surrounding the redox active $VO_x$ species present on the solid increases.[71]

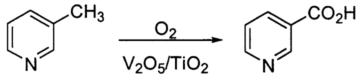
acrolein

Although vanadium ions present on vanadium oxide act generally as redox sites, when supported on zirconia and titania they act as well as Lewis acid sites strong enough to form $\pi$ complexes with toluene and *m*-xylene as evidenced by IR spectroscopy.[72] The methyl group of these $\pi$ complexes becomes activated and undergoes hydrogen abstraction by the V=O group leading to benzylic species and benzaldehyde.[72] On the other hand, phenol is adsorbed through the oxygen atom and the phenyl ring is oriented perpendicular to the solid surface. Benzene is adsorbed forming mono and dimeric species.[72]

Lateral chain oxidation of alkylaromatics is an industrial process of paramount importance that can be also catalyzed by vanadium oxides.[73] Acidity also seems to play a role in this process, facilitating the oxidation. $V_2O_7/TiO_2$ doped with K, Ba, Bi, W, and Sn oxides or carbonates exhibits catalytic activity in the oxidation of *ortho*-xylene to phthalic anhydride. At reaction temperatures higher than 370 °C, good correlation between the strength of the acid sites and phthalic anhydride yield (K < Ba < Bi < unpromoted < W ≈ Sn) was observed.[74] A restructuring of the catalyst, resulting in higher V/Ti surface ratios, occurs during the use of $V_2O_7/TiO_2$ in *o*-xylene oxidation without any change in the crystallinity, the crystal size, or the +5 oxidation state of the V ions.[74]

In the heterocyclic version of the alkylaromatic oxidation, picoline can be directly oxidized with excellent yields (98%) by $O_2$ in the gas-phase to nicotinic acid in the presence of $V_2O_5$-impregnated $TiO_2$ (Scheme 7).[75] The latter catalyst contains Brönsted acid sites in addition to redox centers.

**Scheme 7**



Propane ammoxidation to acrylonitrile can be catalyzed by vanadium−antimony mixed oxides.[76] The use of these solids in propane ammoxidation causes the surface +V oxidation state to approach +IV and diminishes the vanadium surface enrichment. This is due to the aggregation of V species and the decrease in the surface density of V oxide.[77]

Mixed Ni−Cr−V, Mg−Cr−V, and Ni−Al−V oxides have been prepared by thermal decomposition of layered precursors of hydrotalcite structure at temperatures between 300 or 500 °C.[78] Surface acidity of the resulting solids was studied by means of the FT-IR monitoring of pyridine adsorption and correlated with the dehydrogenation of 2-propanol to acetone at 300 °C. It was found that this oxidation occurs more extensively on Cr-containing mixed oxides due to the lack of Brönsted acidity and the exclusive presence of Lewis acid sites.[78] The results have been correlated again with the operation of the Mars and van Krevelen mechanism.

In general, it can be summarized from the above two sections that vanadium phosphates and supported vanadium oxide are the solids of choice for alkane oxydehydrogenation and oxygenation in the gas phase. However, for oxidations in the liquid phase there is a considerable leaching of vanadium species from the solid to the solution. These dissolved vanadium species are responsible for most of the catalytic activity observed in solution. Attention has to be paid when trying to detect the leached vanadium species, since after cooling the reaction mixture, they can redeposit on the solid that will act as a reservoir for soluble catalytically active species.

This lack of catalyst stability of vanadium-containing solid will be also commented on in the next sections and is the reason that despite the inherent activity of vanadium for catalytic oxidations, the use vanadium-containing solids has not been expanded to liquid-phase reactions. Although vanadium is by far the most important transition metal for hydrocarbon oxygenations, many other metal oxides have also been used as oxidation catalysts, and this will be discussed in the next section.

### *2. Metal Oxides Other than Vanadium*

Compared to zirconia, sulfated zirconia exhibits also oxidizing properties giving rise to the formation of phenol and trimethylphosphane oxide by adsorption of benzene and trimethylphosphane, respectively.[79−81] These two oxidative processes are something that is not observed for sulfate-free zirconia.[81] The reaction mechanism has been firmly correlated to the intermediacy of radical cations generated through electron transfer from the organic compound to sulfated zirconia. EPR spectroscopy provides some evidence suggesting the formation of $SO_3^{\bullet-}$ radical anion during the oxidation of trimethylphosphane oxide.[80,81]

Analogously to sulfate, it has been found that the addition of just a small amount of chromium oxide (1 wt % Cr) to zirconia increases remarkably both the number and strength of the acid sites.[82] Characterization indicates the presence of both Brönsted and Lewis acid sites on the surface of $CrO_x/ZrO_2$ and that the oxidation state of Cr can change reversibly between Cr(VI) and Cr(III).[82]

Supported metal catalysts are widely used for the partial oxidation of alkanes or alcohols. The catalytic effects are not only due to changes in the metal dispersity but also to the interaction of the metal with the Lewis acid sites of the support. Experimental evidence indicates that the support and modifiers or promoters play a pronounced influence on the oxidation state of the metal atoms, ions, or partly charged clusters. Some additives exert an electron seeking effect on the metal surface state, stabilizing ionic states and increasing the effective charge of the metal ions, favoring their fast reduction during the catalytic cycle. For instance, while platinum deposited on alumina forms a platinum compound on the solid surface, the weaker electron acceptor properties of charcoal compared to alumina determines that the species present on charcoal surface is predominantly metallic platinum.[83]

The active oxidation states of supported metal catalysts, such as Cu, Ag, and Au can be discussed by IR spectroscopy, UV−Vis spectroscopy, XRD, XPS, EXAFS, and electron microscopy. Comparison of the catalytic and the spectroscopic data reveals that metal cations are the active sites of the metal catalyst surface in alcohol oxidation.[84]

High temperature methanol chemisorption and in-situ IR spectroscopy have been used to determine quantitatively the number of active sites available for methanol oxidation in bulk mixed metal molybdates.[85,86] It was found that Mo atoms are the sites in which methanol are bound and that the activity of the mixed metal molybdates decreases with the increase in the accompanying cation electronegativity due to electronic variations on the metal−O−Mo bonds. The same effect is observed for supported metal oxides.[85,86]

Diffuse reflectance FTIR spectroscopy has been used to investigate the influence of the solid composition and treatment on the population and relative proportion of Brönsted/Lewis acid sites of silica−alumina supported Mo oxide catalysts.[87] It was found that the ratio Brönsted-to-Lewis acid population increases with the $SiO_2$ content of the support reaching a maximum for silica−alumina 75:25 or for alumina-rich supports this ratio also increases with the $MoO_3$ loading.[87] Analogously, EPR spectroscopy supports that Ce(IV) ions not fully coordinated are responsible for the Lewis acidity of ceria and $CeO_2$ supported on silica.[88] The matrix influences the cerium distribution and the electron-acceptor redox properties of coordinatively unsaturated Ce(IV) ions.[88]

IR titration using pyridine as base has shown that silica-, alumina-, and zirconia-supported tantalum oxide are considerably more Lewis acidic than analogous vanadia-supported oxides.[63] Spectroscopic characterization reveals that there may be two different tantalum species present on the surface. Distorted tetrahedral $TaO_4$, having a Ta═O tripodally bound to the solid surface through three single Ta−O− bonds and octahedral $TaO_6$. The former predominates at low coverages. The activity of supported tantalum oxide has been studied as catalyst for methanol oxidation and their performance compared to vanadia.[63]

The activity and stability of solid catalysts for methane-$CO_2$ reforming depend on the formation of carbon deposits due to methane decomposition into C and $H_2$.[89] This carbon deposited on a metal site can be reoxidized to CO by oxygen coming from the dissociation of adsorbed $CO_2$. For noble metals, this oxidation of deposited carbon is fast, leading to low carbon accumulation on the metal particles.[89] What is remarkable is that the rate of carbon formation from methane was proportional to the concentration of Lewis acids. Thus, the combination of Pt with a support with a low Lewis acidity such as $ZrO_2$ was found more suitable for long stability of the catalysts. For nonnoble metals such as Ni, the rate of methane dissociation exceeds the rate of carbon reoxidation to CO, and carbon deposits develop rapidly in the form of filaments. The rate of carbon filament formation was proportional to the Ni particle size and may be interesting for the production of carbon nanotubes.[90,91] Thus, in order for these solids to act as efficient catalysts, it is necessary to reduce the particle size below a critical particle size value ($d$ < 2 nm). Well dispersed Ni supported on $ZrO_2$ is a viable alternative to noble metal-based catalysts for methane-$CO_2$ reforming.[89]

Partial oxidation of propane to syngas has been carried out in a flow reactor using as catalyst nickel oxide supported on alumina, magnesia, and silica.[92] Alumina-supported NiO was found the most suitable catalyst. Modification of these catalysts by alkali metal oxides or rare-earth oxide reduces the strength of the Lewis acid sites, and by decreasing the carbon deposition increases the stability and lifetime of the catalyst during propane partial oxidation.[92]

In the heterogeneous catalytic oxidation of hydrocarbons under mild conditions, the solid oxide catalysts can be viewed as a reagent that is regenerated after each redox cycle.[40] New reactor design like transported bed and membrane reactors have been developed based explicitly on this principle.[40]

In this context, it has been reported that alkali metal doping of transition metal oxides endowed the oxides with the ability to convert $CH_4$ to ethane and ethene. Thus, nickel oxide doped with lithium was an active catalyst for oxidative coupling of methane. On the basis of XRD analysis, it has been proposed that $LiNiO_2$ is the actual solid catalyst. According to eq 1, methane would react to form C-2 products and water with the lattice oxygens of $LiNiO_2$. These structural oxygens would be in turn regenerated by molecular oxygen (eq 1).[93]

$$2CH_4 + 2LiNiO_2 \rightarrow C_2H_6 + H_2O + Li_2O + 2NiO$$
$$Li_2O + 2NiO + {}^1/_2O_2 \rightarrow LiNiO_2 \qquad (1)$$

The influence of the nature of a metal oxide among Ca, Sm, and Yb in mixed oxides with zirconia in equimolar amounts has been studied for the oxidative coupling of methane. The activity of the catalysts is proportional to the specific surface area of the mixed oxide, while the selectivity toward $C_2$ hydrocarbons increases in the series $CaO < Sm_2O_3 < Yb_2O_3$.[94] Characterization has revealed that the solids do not have Brönsted acid sites, but there are three different types of Lewis acid sites. The total concentration of these Lewis sites however follows the reverse order found for the selectivity of these mixed oxides toward the oxidative methane coupling to $C_2$.[94]

The applicability of surface science techniques to obtain insights on the mechanism of heterogeneous reactions catalyzed by metal oxides has been exemplified in the dehydrogenation of ethylbenzene to styrene catalyzed by iron oxide.[95] The information provided by surface science techniques in ultrahigh vacuum has been combined with batch reactor measurements at high pressure.[95] Ethylbenzene and styrene adsorb on regular terrace sites with their phenyl rings oriented parallel to the surface. The $\pi$ electron cloud of the aromatic rings interact with the Lewis acidic atoms on the surface. Atomic defects are identified as catalytically active sites. A complete mechanistic description of the process at the atomic level is proposed in which the upward tilted ethyl group of flat adsorbed ethylbenzene is dehydrogenated at Brönsted basic oxygens located at defects.

The conversion of methane into methyl formate with high molar yields (>12%) has been attained by a two reactor system. In the first one, the partial oxidation of methane to formaldehyde is accomplished at 600−700 °C on $SiO_2$. Subsequently, formaldehyde is dimerized to methyl formate through a Cannizzaro disproportionation at 130−170 °C on various metal oxides, including titania, silica, zirconia, and sulfated zirconia.[96]

Partial oxidation by oxygen of methanol to formaldehyde has been studied over $SiO_2$- or $MoO_3$-supported ferric oxide in supercritical $CO_2$ at 90 bar.[97] Formaldehyde selectivity was found to depend on the percentage of iron on the support, the nature of the support, and the reaction temperature. Compared to silica, molybdenum oxide as support favors the formation of formaldehyde. This higher selectivity is related to the formation of iron molybdate as the active catalytic phase. FT-IR data indicate that the first step in all reaction processes is the generation of adsorbed iron-methoxy species.[97] Molybdena supported on titania prepared from aqueous solutions of ammonium heptamolybdate and titania or by mechanical mixing of both oxides is also very active for the partial oxidation of methanol.[98]

Fine-tuning of the Lewis acid/base properties of the surface pairs has been proposed as the important factor to control the activity and selectivity for the oxidative coupling of methane using solid solutions of rare earth and bismuth oxides.[99] From the catalytic tests in fixed-bed flow reactors, it has been found that the activity toward $C_2$ products increases with catalyst basicity, while an increase in the Lewis acidity of the Bi cation leads to an enhancement of the ethene selectivity.[99]

Sol−gel chemistry using metallic complexes as precursors has been used to prepare Fe−Al mixed oxide exhibiting activity as catalyst for the liquid-phase cumene oxidation. It has been proposed that the mixed oxide acts as a bifunctional catalyst containing Lewis acid sites and terminal O centers.[100] As mentioned for the case of supported vanadium oxides as catalysts for liquid-phase reactions, the possibility of metal leaching and subsequent homogeneous phase catalysis by the leached metal should be addressed in this type of catalyst.

Likewise, heterogeneization of cobalt atoms by simple coprecipitation in the formation of silica gels using $Co(OAc)_2$ has been reported to be effective for the side chain oxidation of alkylaromatic using *tert*-butyl hydroperoxide as oxidant. Diffuse reflectance UV−Vis and IR spectra of the solid seem to support the presence of tetrahedral Co(II) (detached from acetate anions) in the silica framework.[101]

Ozone and several of its $^{18}O$-labeled isotopomers have been adsorbed on metal oxides such as silica, titania, zirconia, magnesia, and ceria at liquid $N_2$ temperature.[102] Ozone behaves as a weak basic molecule and interacts with surface hydroxyl groups. With weak Lewis acid sites, ozone molecules form coordination adducts via a terminal oxygen atom, with stronger Lewis acid sites (such as titania, alumina, and zinc oxide) no evidence of a Lewis adduct is obtained. Apparently, ozone dissociates on these sites generating highly reactive oxygen atoms. These oxygen atoms can participate in the catalytic oxidation of CO on oxide surfaces.[103]

An IR study of adsorbed CO, $NH_3$, $C_3H_6$, $C_3D_6$, and $C_3H_6$-$O_2$ on oxidized and reduced samples of mixed titanium−antimony oxide showed that both oxidized and reduced solids contain basic sites, but lack of strong Lewis acid centers.[104] Interaction of propene occurs through the C−H bond of the methyl group with the basic sites.[104]

Chromium(III) oxide is able to catalyze the disproportionation of chlorodifluoromethane. This reaction can be useful to prepare commercially important fluorinated methanes and apparently takes place on coordinatively unsaturated $Cr^{3+}$ species.[105]

Several solids have been developed for the Meerwein−Ponndorf−Verley−Oppenauer reactions exhibiting the typical advantages with respect to homogeneous catalysts, like easy handling and workup and recycling. A review discussing the use of amorphous metallic oxides and zeolites, particularly Beta and silicalite as catalysts for the Meerwein−Ponndorf−Verley reaction has recently appeared.[106] Amorphous metallic oxides and zeolites that exhibit surface basicity or Lewis acidity are generally the solids used as catalysts for this type of disproportionation.

Layered clays have been extensively used as acid catalysts and as supports for oxidants (clayfen and claycop) and Lewis acids (clayzic).[107−110] Hydrogen cyanide has been proposed as a probe of the Brönsted and Lewis nature of the acid sites in metal-oxide pillared clays.[111] Upon exposure of metal oxide-pillared clay to saturated and unsaturated hydrocarbons, a decrease in the density of sites that interact with HCN is observed by IR spectroscopy.[111] The outcome of this study based on the HCN probe is that while the metal oxide pillars are responsible for the Lewis acidity, the Brönsted acid sites are located on the clay sheets. A third type of site appears in the pillar fixation process. These distinctive sites associated to the pillaring process are most affected by the nature of the pillar and may exhibit selectivity to interact with a hydrocarbon. For example, zirconium oxide pillared hectorite interacts most effectively with benzene or toluene than *n*-hexane or cyclohexane.[111]

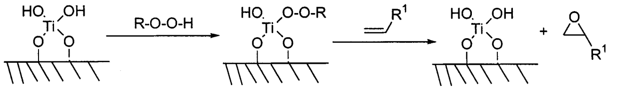
A natural bentonite pillared with aluminum, aluminum−iron, and aluminum−ruthenium polyoxocations has been further ion exchanged with iron.[112] All these solids were active materials for the catalytic transformation of propene into acetone at temperatures between 150 and 350 °C.[112] The reaction proceed via acid-catalyzed propene hydration followed by dehydrogenation of 2-propanol to acetone. Accordingly, the activity of the solids correlates with the nature and population of the redox and acid sites.[112]

K10-montmorillonite and 4A molecular sieves catalyze the oxidation of secondary benzylic alcohols by *tert*-butyl hydroperoxide in good yield and selectivity, except when an electron-donating group is present in the 4-position of the phenyl ring.[113] The reaction mechanism was assumed to involve an Oppenauer-type oxidation. Using zeolite 13X as catalyst, a very enhanced activity was observed and interpreted as reflecting the fact that the reactants can be accommodated inside the zeolite cavities. However, besides the fast formation of carbonylic compounds, other competitive side reactions take place lowering the resulting selectivity.[113]

## C. Oxidations via Lewis Acid−Base Adducts

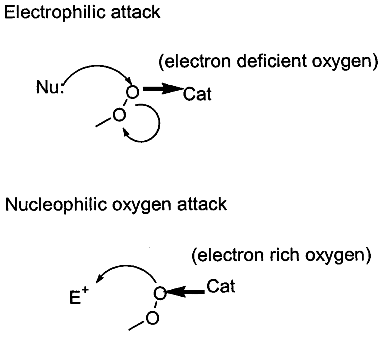
The third general way in which a Lewis acid can catalyze oxidation reactions is by forming an acid−base adduct either with the substrate or with the oxidizing reagent, enhancing their reactivity and thereby acting as catalyst for the oxidation (see chapter II and Scheme 8). A typical example is the olefin epoxidation by titanium-containing zeolites that will be discussed latter. In this type of mechanism, the metal atom does not undergo variation in its oxidation state and the catalysis occurs because tetracoordinated titanium atoms bind to the hydroperoxide and enhance the electrophilicity of this oxidant. Thus, while TS-1 was initially described as a redox catalyst, it is now being increasingly recognized “simply” as a Lewis acid solid.[114]

**Scheme 8**

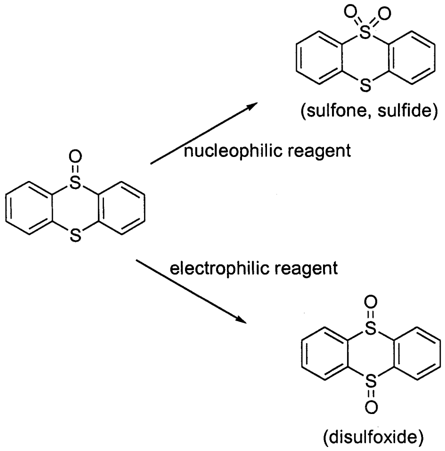


Comparison of the oxidation rates using as substrate a sulfide and the corresponding sulfoxide can be used to distinguish the electrophilic or nucleophilic nature of the catalytically relevant active species (Scheme 9). Thianthrene oxide has been proposed as a probe molecule for this purpose (Scheme 10).[115,116]

**Scheme 9**



**Scheme 10**



This type of study allows one to gain insight into the oxygen atom insertion process (either electrophilic or nucleophilic) and on the role and optimum structure of the catalyst. Thus, for instance, similar reaction rates have been measured for the oxidation of methyl *p*-tolyl sulfide and the corresponding sulfoxide by cumyl peroxide using titanium(IV)-(*R*,*R*,*R*)-tris(2-phenylethoxy)amine as catalyst.[117] Such behavior stands in contrast with the remarkably high selectivity exhibited by $d^0$ transition metal peroxo complexes. This has led to the conclusion that the alkylperoxo complex formed by the attack of the cumyl hydroperoxide to the titanium catalyst is the actual catalytic species. This alkylperoxo displays a biphilic nature, behaving as electrophilic oxidant toward the sulfide and nucleophilic oxidant when it reacts with the sulfoxide. Theoretical calculations (RHF/3-21G*) and kinetic evidence indicate that the Lewis acidity of the Ti(IV) metal center activates the hydroperoxide and the sulfoxide in a template intramolecular process.[117]

All Lewis acid catalysts active in the selective oxidation of hydrocarbons contain transition metal cation of $d^0$ or $d^{10}$ configuration. The interaction of weakly basic unsaturated hydrocarbons with transition metal ions has been considered as "weak base" (hydrocarbon)–"strong acid ($d^0$ cations)", or "weak base" (hydrocarbon)–"weak acid" ($d^{10}$ cations) interactions.[118−120] Taking this into account, the selectivity of the oxidation will depend on the activity of the transition metal and decreases in the order indicated in Scheme 11.[118]

**Scheme 11**

$d^0$

$V^{5+} > Mo^{6+},\ W^{6+} > Nb^{5+},\ Ta^{5+} > U^{6+},\ V^{4+} > Ti^{4+} > Zr^{4+} > Th^{4+} > U^{4+}$

$d^{10}$

$Sb^{5+} > Sn^{4+} > Pb^{3+} > Sb^{3+} > Bi^{3+} > Pb^{2+} > Cu^{+} > Ag^{+}$

It appears then that the adsorption and activation of hydrocarbons in oxidation processes can be regarded as acid–base interactions.[121] In this sense, a too strong adsorption of hydrocarbon on the oxidation acid sites will result in a too long contact time on the surface with the corresponding loss of selectivity. The hallmark of these Lewis acid catalyzed oxidations is that the oxidation state of the metallic ion does not change during the catalytic cycle. This occurs typically in catalytic oxidations that follow a mechanism in which the oxygen transfer occurs via peroxometallic intermediates:[122,123] Transition metals that react through peroxometalic species are Ti, Zr, Mo, and W.

With respect to the oxidating agents, the production of bulk products involves the use of air or oxygen. However, when the added value of the product increases, then other oxidants with a higher cost can be used. In Table 1 different oxidants are presented together with the active oxygen content and the corresponding byproduct formed.

**Table 1. List of Oxidizing Reagents that Can Be Used in Catalytic Reactions**

| oxidant | % active oxygen | subproduct |
|---|---|---|
| $H_2O_2$ | 47.0 | $H_2O$ |
| $N_2O$ | 36.3 | $N_2$ |
| $O_3$ | 33.3 | $O_2$ |
| $CH_3CO_3H$ | 26.6 | $CH_3CO_2H$ |
| t-$BuO_2H$ | 17.8 | t-BuOH |
| NaClO | 21.6 | NaCl |
| $NaClO_2$ | 19.9 | NaCl |
| NaBrO | 13.4 | NaBr |
| $HNO_3$ | 25.4 | $NO_X$ |
| $C_5H_{11}NO_2$ | 13.7 | $C_5H_{11}NO$ |
| $KHSO_5$ | 10.5 | $KHSO_4$ |
| $NaIO_4$ | 7.0 | NaI |
| PhIO | 7.3 | PhI |

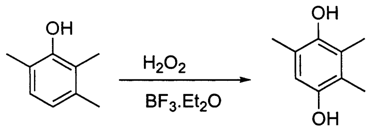
In this following section, we will show the logical evolution from homogeneous Lewis acid catalysts, supporting them on solid supports and finally developing an efficient isotropic solid Lewis acid catalyst containg framework transition metals.

### *1. Oxidations in Homogeneous Phase*

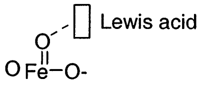
There are plenty of examples in which Lewis acids catalyze oxidation reactions by coordinating either with the substrate (increasing its electron deficiency) or with the oxidizing reagent (enhancing its electrophilicity). The catalysis occurs truly through an acid/base mechanism. However, since the outcome of the reaction is the oxidation of a substrate, some misleading rationalization can describe these Lewis acids as redox catalysts. This misconception has been particularly frequent when the catalyst is a solid Lewis acid. The following examples in homogeneous phase have been selected to illustrate that Lewis acid assistance of oxidation reactions is very well established in solution.

**a. Use of Conventional Lewis Acids.** A Japanese patent describes the preparation of 2,3,5-trimethylhydroquinone, an intermediate in the synthesis of vitamin E,[124] by catalytic oxidation of 2,3,6-trimethylphenol by hydrogen peroxide in the presence of boron trifluoride etherate or sulfuric acid using methyl ethyl ketone as solvent (Scheme 12).[124]

**Scheme 12**



It has been found that the presence of just a few equivalents of Lewis acids such as boron trifluoride or aluminum trichloride accelerates considerably the room-temperature oxidation of alkanes with chromate or permanganate.[125] In this context, cyclohexane can be oxidized at room temperature by barium ferrate,[126] permanganate,[125] chromate[125] in a mixture of acetic acid and dichloromethane giving a product distribution containing cyclohexanol, cyclohexanone, and cyclohexyl chloride. The reaction requires the presence of a Lewis acid. Among the series of Lewis acids tested, the oxidation rate follows the order $AlCl_3$ > $FeCl_3$ > $MgCl_2$ > LiCl > $ZnCl_2$. This system is also able to oxidize ethane and propane to give mixtures of chloroalkanes and carbonylic compounds. It was proposed that in the case of ferrate the active intermediate is the Lewis acid adduct formed by coordination of an oxo ligand of the ferrate to the Lewis metal center. This adduct initiates the oxidation by abstracting one hydrogen atom from the alkane and generating a carbon-centered radical. Also barium ruthenate in acetic acid-dichloromethane oxidizes alkanes at room temperature with appreciable rates and yields, the reaction being remarkably accelerated by the presence of a few equivalents of Lewis acids.[127]

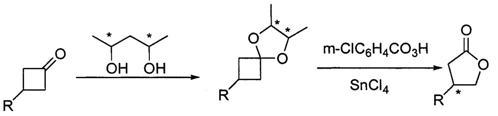


ferrate adduct

The Baeyer–Villiger oxidation transforms aldehydes into carboxylic acids or ketones into esters by reaction with carboxylic peracids. Despite the availability of carbonylic compounds, the potential of the Baeyer–Villiger reaction in organic synthesis remains underdeveloped due to the lack of chemoselectivity when other functional groups, particularly C=C double bonds, are also present in the molecule.

The development of catalytic versions of the Baeyer−Villiger can help to overcome the limitation of poor selectivity. An example of asymmetric Baeyer−Villiger reaction for the formation of *β*-substituted *γ*-butyrolactones based on the concept of chiral auxiliary has been reported.[128] The process consists of using an enantiomerically pure acetal as the starting material for the Baeyer−Villiger oxidation. The acetal is prepared from the achiral 3-substituted cyclobutanone and enantiomerically pure 2,5-pentanediol. Oxidation is carried out at low temperatures (−78 °C) using *m*-chloroperbenzoic acid assisted with $SnCl_4$ as catalyst (Scheme 13).[128]

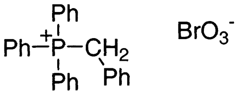
**Scheme 13**



The oxidation of sulfides to sulfoxides by permanganate in anhydrous acetone solutions has been shown to be catalyzed by Lewis acid such as $FeCl_3$, $ZnCl_2$, and $HgCl_2$.[129] The kinetics unequivocally confirm that the function of the Lewis acid is to activate the oxidant by forming a permanganate/Lewis acid adduct analogous to the protonation of $MnO_4^-$ by Brönsted acids. A Hammett analysis of the reaction rate constant in a series of substituted thioanisoles gives a negative $\rho$ value, indicating an electron deficient transition state. All the kinetic data including secondary kinetic isotopic effect and sulfide/sulfoxide competitive oxidation are consistent with a mechanism in which the oxidant and the reductant react via initial ligation.[129]

Sodium and silver bromates ($NaBrO_3$ and $AgBrO_3$) are stoichiometric oxidizing reagents in organic solvents for a variety of organic functional groups provided that the oxidation is assisted by Lewis acid catalysts. Among the compounds that can be oxidized are alcohols, acyloins, hydroquinones, and aldehydes. Primary benzylic C−H are oxidized to aromatic carboxylic acids, while secondary C−H are oxidized to ketones.[130] A heterogeneous version of this process uses Amberlite IRA-400 supported bromate, and the system has the advantage of being regenerated.[131]

An analogous bromate reagent is benzyltriphenylphosphonium bromate, prepared by ion metathesis from benzyltriphenylphosphonium chloride with sodium bromate.[132] The quaternary phosphonium counteranion renders bromate more soluble in organic solvents. This oxidizing reagent is thermally stable and in the presence of Lewis acid catalysts can be utilized to oxidize efficiently in organic aprotic solvents. This bromate salt converts benzylic alcohols, cycloalcanols, and hydroxyketones into the corresponding carbonyl compounds in good yields and thiols to disulfides in moderate yields.[132]



benzyltriphenylphosphonium bromate

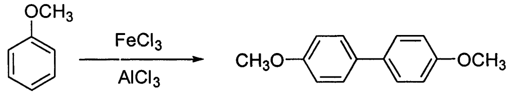
Benzyltriphenylphosphonium periodate has been prepared in the same way as the corresponding bromate and exhibits a parallel behavior. Its use as oxidant reagent also requires the assistance of a Lewis acid.[133] Thus, for instance, aluminum trichloride or boron trifluoride etherate are active catalysts for the oxidation by tetrabutylammonium periodate of a series of organic compounds such as alcohols to carbonyl compounds, α-hydroxyketones to diketones, and α-hydroxycarboxylic acids to carbonyl compounds after decarboxylation, thiols to disulfide, and thioethers to sulfoxides.[134]

Primary and secondary benzylic and saturated trimethylsilyl ethers are efficiently converted to the corresponding carbonyl compounds with silver bromate assisted by $AlCl_3$.[135] *p*-Hydroquinone trimethylsilyl ether is also converted to *p*-benzoquinone with either $AgBrO_3/AlCl_3$ or with $NaBrO_3/AlCl_3$. $AgBrO_3/AlCl_3$ is able to oxidize primary trimethylsilyl ethers to their carboxylic acids. Primary and secondary benzylic trimethylsilyl ethers are also converted to their carbonyl compounds with $NaBrO_3/AlCl_3$. $AgBrO_3$ is more efficient and selective than $NaBrO_3$.[130]

Thiophenes treated with *m*-chloroperbenzoic and boron trifluoride etherate form S-monoxide intermediates that undergo in situ cycloaddition with dienophiles to give the corresponding cycloadducts.[136] The presence of the Lewis acid enhances considerably the yield of the oxidative cycloaddition. Moreover, a larger number of dienophiles react with thiophene S-oxide giving cycloaddition when the Lewis acid is present.[136]

$FeCl_3$-promoted oxidative coupling of methoxyarenes to form the corresponding biaryls is significantly enhanced in the presence of stoichiometric amounts of $AlCl_3$, whereby yields between 28 and 85% with excellent selectivity are obtained (Scheme 14).[137]

**Scheme 14**



Primary and secondary aliphatic alcohols and aromatic lateral chains can be air oxidized using *N*-hydroxyphthalimide and Lewis acids such as $BF_3$ as cocatalysts.[138] The role of the Lewis acids is to weaken the O−H bond of the hydroxylimide through hydrogen bond formation, favoring the homolytic O−H bond breaking. The oxidation occurs through a chain reaction mechanism initiated by the nitroxyl radical derived from the hydroxyphthalimide.[138]

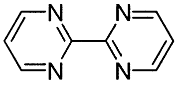
From the previous examples, it can be concluded that the phenomenon of the assistance of oxidation reactions by conventional Lewis acids ($AlCl_3$, $BF_3$, etc.) is quite general and well established in liquid phase. We will follow showing that transition metals behaving as Lewis acids are also homogeneous oxidation catalysts.

**b. Use of Soluble Transition Metals and Transition Metal Complexes.** Transition metal ions are also Lewis acids that can bind to oxidizing reagents and in this way catalyze oxidation reactions.

Hydroperoxides are widely used as environmentally acceptable oxidizing reagents. In the presence of an aqueous carbonate solution as buffer, simple manganese(II) salts, such as $MnSO_4$, catalyze alkene epoxidations.[139] The epoxidations are carried out at room temperature by dissolving the alkene and manganese salt in dimethylformamide or *tert*-butyl alcohol and slowly adding 30% $H_2O_2$ and 0.2 M sodium bicarbonate buffer. Among the obvious advantages of this homogeneous epoxidation process, besides the use of hydrogen peroxide as oxidizing reagent, the major one is the use of an inexpensive and off-the-shelf available catalyst that does not contain or require sophisticated organic ligands. Since bicarbonate is a necessary additive, it is proposed that the reaction mechanism involves the intermediacy of hydrogen percarbonate as the active oxidant.[139] Obviously, despite its simplicity the drawback of this homogeneous process is the impossibility to recycle the catalyst and the production of manganese byproducts in the oxidation, although in substoichiometric amounts.

Electron-rich aromatic compounds can be brominated with KBr and $H_2O_2$ using $V_2O_5$, $Mo_7(NH_4)_6O_{24}$, or $NH_4VO_3$ as catalysts.[140] Reexamination of this reaction has shown that the process consumes stoichiometric amounts of an acid such as sulfuric acid. The system NaBr or KBr, diluted mineral acid (HCl, $H_2SO_4$, $HNO_3$, or $H_3PO_4$) and hydrogen peroxide in the presence of divanadium pentoxide has been proposed as an alternative to other bromination reagents.[141]

Lower alkanes such as methane can be catalytically oxidized into esters in the liquid phase using a media that combines very strong acidity and oxidation activity such as sulfuric acid using stable Pt-2,2′-bipyrimidine complexes as catalysts and tellerium or antimony salts as cocatalysts.[142]



2,2’-bipyrimidine

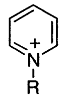
Aqueous solutions of transition metals can catalyze aerial oxidation of substrates in a different phase. Thus, isomerized kerosene−gas oil fraction at 170 °C under pressure in the presence of an aqueous solution of transition metal carboxylates, particularly cobalt(II), undergoes oxidation to high-purity succinic acid that crystallizes from the aqueous solution.[143]

Lateral chain oxidation of alkylaromatics to aromatic carboxylic acids is an industrial oxidation of huge economic importance that can be effected by transition metal catalyzed oxidation using oxygen as oxidant. Thus, a process for the manufacture of benzoic acid and its salts in which a quaternary ammonium bromide facilitates the oxidation of toluene has been reported.[144] In this process, the quaternary ammonium ion acts as phase transfer catalyst and the oxidation occurs at about 150 °C and high pressure of oxygen (12−15 atm) in the presence of catalytic amounts of a transition metal salt such as $CoCl_2$ dissolved in water.[144] Terephthalic acid can also be obtained through liquid-phase oxidation of *p*-phenylene compounds catalyzed by transition metal compounds.[145]

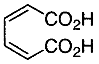
2,6-Diisopropyl- and related 2,6-dialkylnaphthalenes can be oxidized by air oxygen under pressure in a batchwise manner using a mixture of $Cu(OAc)_2$, $Mn(OAc)_2$, and KBr as catalyst and acetic acid as solvent to form 2,6-naphthalenedicarboxylic acid with high yields.[146] Likewise, 1,4-naphthalenedicarboxylic acid was also prepared by oxidation of 1,4-dialkylnaphthalenes with oxygen using as catalyst a solution of transition metal in acetic acid.[147] 1,4-Naphthalenedicarboxylic acid is an important starting material for the production of polyesters.

The target in the vast majority of oxidations using organic hydroperoxides is to obtain a valuable oxidized product, hydroperoxides being considered as reagent. An exception to this is the case of cyclohexyl hydroperoxide formed in large scale quantities in the oxidation of cyclohexane with oxygen. To process cyclohexyl hydroperoxide, it has been proposed the use of cyclohexene soluble transition metal compounds to catalyze the epoxidation of cyclohexene. Subsequently, the resulting cyclohexene oxide is reduced to cyclohexanol or transformed to other valuable cyclohexane derived product.[148]

A process to obtain highly pure 1,1′-dialkyl-4,4′-bipyridinium salts from 1-alkylpyridinium ions consists of the coupling of the latter in the presence of alkali cyanide[149] in aqueous methanol, followed by removing the cyanide ion as a divalent transition metal cyanide. Colloidal or supported Cu(II) and Fe(III) hydroxides catalyze at room temperature in aqueous hydrogen peroxide solutions the oxidation of catechol to muconic acid and benzene to phenol.[150]



N-alkylpyridinium

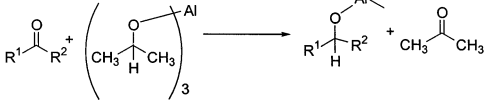


*c,c*-muconic acid

In the classical Meerwein−Ponndorf−Verley reaction, a carbonylic compound becomes reduced using 2-propanol as solvent and reducing agent in the presence of aluminum isopropoxide as catalyst (Scheme 15).[151] Alkali metal alkoxides are inefficient to promote this formal hydride transfer. The same reaction, but now considered as the selective oxidation of a secondary alcohol to a ketone, is known as the Oppenauer oxidation. Quantitative information about the equilibrium of a given Meerwein−Ponndorf−Verley−Oppenauer reaction can be obtained from thermodynamic data.

The reaction mechanism of the Meerwein−Ponndorf−Verley−Oppenauer reactions has been reviewed.[152] Mechanistically, the Meerwein−Ponndorf−

**Scheme 15**



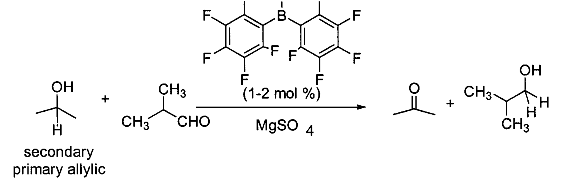
Verley−Oppenauer reaction is an example of an oxidation or reduction equilibrium that is catalyzed by a Lewis acid. These processes are related to the Cannizzaro disporportionation since the key step is a hydride transfer from a donor to an acceptor. In the case of the Meerwein−Ponndorf−Verley−Oppenauer, the reaction generally proceeds through a six-membered transition state in which both reductant and oxidant are coordinated to the metal center of a metal alkoxide catalyst. In aluminum-catalyzed reactions, ligand exchange is always the rate determining step, and it can be so slow that it precludes the use of aluminum alkoxides in catalytic amounts.

More promising as homogeneous Meerwein−Ponndorf−Verley−Oppenauer catalysts are lanthanide, zirconium, or hafnium complexes, which combine strong Lewis acid character and good ligand exchangeability. In lanthanide-catalyzed reactions, the ligand exchange is much faster and the reaction rate is dominated either by ligand exchange or by the hydride transfer step.

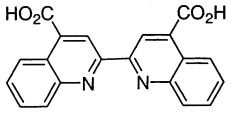
The catalytic activity of lanthanide isopropoxides increases in the order La < Nd < Gd ∼ Er ∼ Yb, which follows the sequence of metal ion size, indicating that the Lewis acidity of the lanthanide catalysts is the major factor in the Meerwein−Ponndorf−Verley−Oppenauer reactions.[153] Metal alkoxide catalysts can be prepared from the metal halides by alcoholysis.[152] High enantioselective Meerwein−Ponndorf−Verley−Oppenauer reduction in which the catalyst was a chiral lanthanide(III) alkoxide has been reported.[152]

The Oppenauer oxidation is a useful method to transform secondary alcohols into ketones. However, it is in general difficult to apply this reaction to convert primary alcohols into aldehydes. It has been found that bis(pentafluorophenyl)borinic acid at a catalyst/substrate ratio between 1 and 2 mol % is a suitable catalyst to oxidize secondary as well as primary allylic and benzylic alcohols to the corresponding ketones or aldehydes (Scheme 16).[154] Pivalaldehyde was used as hydride acceptor and magnesium sulfate was present as drying agent. The reaction was performed at room temperature. Apparently, the stronger Lewis acidity of perfluorinated diarylborinic acid compared to analogous pentafluorophenylboronic is the most important factor responsible for the catalytic activity of the former compounds.[154]

**Scheme 16**



A water-soluble $[Ir(COD)Cl]_2$ catalyst (COD: cycloctadiene) in combination with 2,2′-biquinoline-4,4′-dicarboxylate has been found highly efficient for the selective Oppenauer oxidation of secondary benzylic and aliphatic alcohols to the corresponding ketones at a catalyst/substrate ratios ranging between 0.4 and 2.5%.[155]

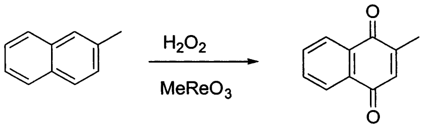


2,2'-biquinoline-4,4'-dicarboxylic acid

Methyl trioxorhenium has been found a robust catalyst to effect epoxidations and alcohol oxidations using hydrogen peroxide as oxidizing reagents.[156−159] Because of its Brönsted acidity, the addition of pyridine and its derivatives can have a positive effect, trapping hydronium ions that may be produced in the reaction with $MeReO_3$. It has been observed that the binding constant of pyridines and methyltrioxothenium is governed by electronic and steric effects. For instance, the binding constant of parent pyridine is 200 L $mol^{-1}$, whereas that of a better electron donor 4-picoline is 730 L $mol^{-1}$ and that of sterically encumbered 2,6-di-*tert*-butylpyridine is lower than 1 L $mol^{-1}$.[160] Pyridine stabilizes the $MeReO_3/H_2O_2$ system by decreasing the steady-state concentration of free $MeReO_3$. The presence of these nitrogen heterocycles considerably reduces the rate of epoxide ring opening having a beneficial influence in the selectivity of the alkene epoxidation catalyzed by $MeReO_3$.[160] Thus, pyridine accelerates the rate of epoxidation of α-methylstyrene, while avoiding the problems derived from the acidity of $MeReO_3$.

Methyltrioxorhenium at 1 mol % is able to catalyze the selective oxidation of electron-rich aromatic compounds to the corresponding quinones using hydrogen peroxide as oxidant and a mixture of acetic acid and anhydride as solvent.[159] Apparently, the anhydride acts as dehydrating agent during the reaction avoiding the interference of the water that is formed as product. As an example, 2-methylnaphthalene is oxidized at 60 °C to give 2-methyl-1,4-naphthoquinone with 87% conversion and 92% selectivity (Scheme 17).[159]

**Scheme 17**



Alkenes can be oxidized into the corresponding carboxylic acids via bond cleavage by $H_2O_2$ using methyltrioxorhenium and $HBF_4$ as cocatalyst.[158]

Cyclopentadienyl trioxorhenium is able to effect the stoichiometric oxidative rearrangement of the ring in a series of alkyl substituted cyclopropenes.[161] The reaction mechanism has been rationalized in terms of an initial alkene−metal interaction, followed by formation and fragmentation of a metallaoxetane. In contrast, phenyl substituted cyclopropenes rearrange in the presence of cyclopentadienyl trioxorhenium to indenes, a process that is catalytic from the point of view of the rhenium and based on the behavior of other Lewis acids is explained in terms of a Lewis acid-catalyzed reaction.[161] Obviously, the problem inherent to the use of soluble rhenium compounds as oxidation catalysts is that despite their remarkable activity they cannot be reused.

cyclopentadienyl
trioxorhenium

The study of the effect of bidentate ligands on the olefin epoxidation using molybdenum oxobisperoxo complexes L-LMoO$(O_2)_2$ has served to establish the relationship between the Lewis acidity and the catalytic activity for epoxidation. This relationship supports an epoxidation mechanism in which the peroxo complex activates the oxidizing agent, either $H_2O_2$ or ROOH, rather than directly transferring an oxygen atom from the peroxo ligand to the olefin.[162] Proton transfer is one of critical points in the catalytic activity of such complexes in olefin epoxidation. NMR studies of proton transfer from strong Brönsted and Lewis acid to L-LMoO$(O_2)_2$ proves that protons are transferred preferentially to the 2-peroxo and not to the oxo ligand.[163]

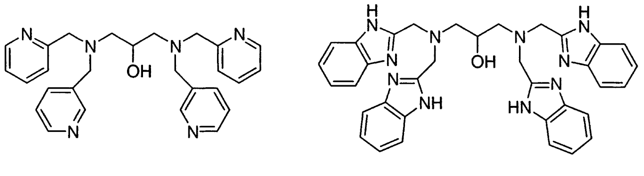
Cerium ammonium nitrate is an strong oxidizing reagent that can effect the stoichiometric oxidation of alkylaromatics to benzylic alcohols and nitrates and primary alcohols to aldehydes.[164,165] Cerium ammonium nitrate can even oxidize methanol. The stoichiometry of the process indicates the concurrent formation of protons during the methanol oxidation. It is believed that these protons are responsible of the cerium ammonium nitrate-catalyzed methanolysis of allylic and benzylic alcohols.[166] This reaction can also be catalyzed equally well by other Lewis acids, thus, reinforcing the assumption that cerium ions intervene as Lewis acids in this alcoholysis.[166]

Benzyl esters are formed catalytically at moderate temperatures from alkyl benzenes using sodium bromate as oxidant and cerium ammonium nitrate as catalyst in a carboxylic acid as solvent.[167] Thus, toluene gives benzyl acetate in acetic acid. Ethylbenzene, cumene, 4-*tert*-butyltoluene, and 4-bromotoluene behave similarly. Xylenes undergoes a selective monoacetoxylation. The cerium salts not only promote the oxidation, but they also act as a Lewis acids that catalyze the conversion of benzyl bromides into the benzyl esters.

Metallic complexes with achiral or chiral ligands are widely used as homogeneous oxidation catalysts. Remarkable examples in terms of selectivity have been reported, the problem being always the impossibility of catalyst recovering and reuse in homogeneous phase. In the following, we will comment on some examples of complexes in the homogeneous phase in which acidity has been found to play a role in catalytic oxidations.

Fluorination of 2,2′-dihydroxy-1,1′-binaphthyl increases the electrophilic character of *tert*-butyl hydroperoxide (TBHP) or cumyl hydroperoxide coordinated titanium center in the sulfide oxidation to sulfoxide.[168] Surprisingly, under identical conditions, the titanium-catalyzed sulfide oxidation using 2,2′-dihydroxy-1,1′-binaphthyl or its 5,5′,6,6′,7,7′,8,8′-octafluoro derivative of the same absolute configuration leads to opposite sense of chiral induction.[168]

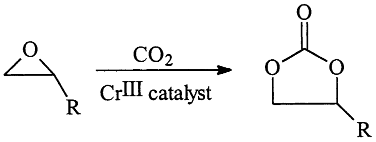
Binuclear Fe(III) complexes derived from *N*,*N*,*N*′,*N*′-tetrasubstituted 1,3-diaminopropan-2-ol having *N*-(2-pyridylmethyl) or *N*-2-benzimidazolylmethyl substituents exhibit a high reactivity as catalysts for the reaction of phenol and 2′-deoxyribose with hydrogen peroxide. The active oxidizing species possesses an electrophilic character. It was proposed that the Lewis acidity of Fe(III), and the steric hindrance imposed by the ligand play a role in the reaction mechanism.[169]



1,3-diaminopropan-2-ol derivatives

Aimed at the search of a reaction for the efficient fixation of $CO_2$, a new catalytic system using chromium(III) bis(salicylaldimine) as catalyst and 4-(*N*,*N*-dimethylamino)pyridine as cocatalyst has been reported.[170] The process gives high yields of cyclic carbonates from the coupling of epoxides and $CO_2$ at 50 psig pressure (Scheme 18). A variety of terminal epoxides including aliphatic and aromatic and epichlorhydrin affords the corresponding carbonates in near quantitative yield and complete selectivity. The catalyst is air stable, maintains its activity over a long reaction time, and does not require any solvent.[170]

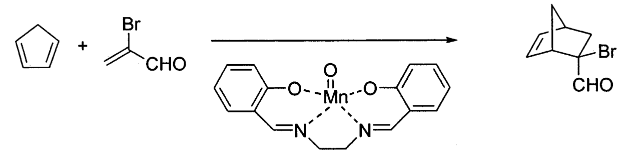
**Scheme 18**



Soluble titanium alkoxides can act as homogeneous epoxidation catalysts in various solvents.[171−173] For instance, homogeneous phase catalytic epoxidation of cyclooctene to form cyclooctene oxide by *tert*-butyl hydroperoxide has been reported in supercritical $CO_2$ using supercritical $CO_2$-soluble Ti$(OCHMe_2)_4$ as catalyst.[174] Following the work of Sharpless and Katsuki on the enantioselective epoxidation of allylic alcohols using chiral titanium complexes of diethyl tartrate,[175−178] Jacobsen and Katsuki reported a series of chiral Mn (III) complexes with Schiff bases as enantioselective epoxidation catalysts for alkenes.[179−181]

In this enantioselective catalytic epoxidation of olefins by alkyl hydroperoxides or other related oxidizing agents, optically active oxo(salen)manganese(V) complexes are the key reaction intermediate in the oxygen atom insertion step. At temperatures

**Scheme 19**

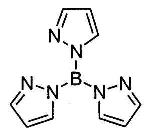


below −78 °C, the oxygen atom insertion ability of this oxo(salen)manganese species is suppressed and, under these conditions, they act exclusively as chiral Lewis acid catalysts for the Diels Alder cycloaddition of cyclopentene with α-bromoacrolein, giving the corresponding cycloadduct in 68% enantiomeric excess and with high *exo* selectivity (Scheme 19).[182]

A case of highly chemoselective oxidation of allylic alcohols to enones has been reported as a function of the (salen)Cr(III) counteranion using iodosobenzene as oxidant.[183] When $Cl^-$ is the (salen)$Cr^+$ counteranion the chemoselectivity to enones is excellent, while for triflate and hexafluorophosphate nearly equal amounts of enone and the epoxy alcohol are obtained. This influence of the counteranion on the oxidation of allylic alcohols mediated by (salen)$Cr^+$ complexes has been rationalized in terms of Lewis acid catalysis by the complex when $Cl^-$ is the counterion and redox catalysis in the case of $CF_3SO_3^-$ and $PF_6^-$.[183]

A review has recently appeared in which the ability of biomimetic metal complexes of Co(II), Fe(II), and Mn(II) derived from open chain $N_2O_2^{2-}$ and macrocyclic $N_4^{2-}$ Schiff base ligands to bind and activate dioxygen has been discussed.[184] Oxygen binding has been correlated with the activity of these complexes to catalyze the oxidation of hydroquinone by $O_2$. In general, catalytic activity is only observed for those complexes that are able to bind oxygen at the central metal atom in the +II oxidation state, although the observed differences in activity could not be rationalized by differences in the oxidation potentials and/or Lewis acidity of the central metal ions. Iron and manganese complexes with some special peripheral substituents reduce dioxygen completely to oxide giving oxygenated oxo derivatives.[184]

By means of sterically encumbered tris(pyrazolyl)borate as ligand, the way in which cobalt complexes activates dioxygen has been found. Initially, a peroxo dimer is formed that gives rise to the oxocobalt complex. Other oxidants such as $N_2O$ forms the hydroxycobalt active species.[185]

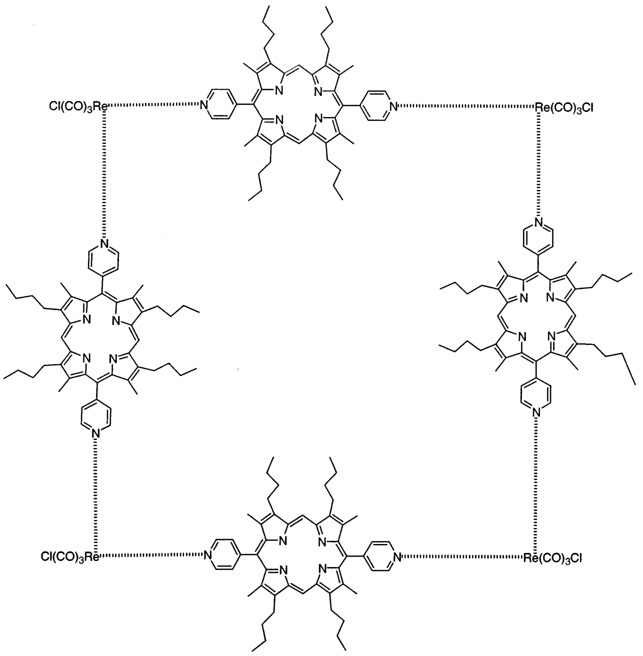


tris(pyrazolyl)borate

Metalated porphyrins have been used as catalysts for the degradation of lignin in wood or pulp, hydroxylation of (cyclo)alkanes, and epoxidation of alkenes by TBHP[186] or iodosobenzene.[187] The use of perchlorinated porphyrins increases the stability of these compounds as catalysts.[188,189]

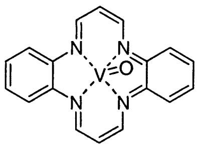
The oxo transfer ability from the nitro ligand to alkenes using (nitro)(pyridyl)cobalt(III) tetraphenylporphyrin has been investigated as a function of the apical pyridine ligand either 4-*N*,*N*-dimethylaminopyridine or 3,5-dichloropyridine.[190] Very modest differences were observed for hexacoordinated complexes, while oxo transfer occurs rapidly through the pentacoordinated species (nitro)cobalt(III) tetraphenylporphyrin generated by dissociation of the pyridine ligand in the hexacoordinate complex. Pentacoordinated (nitro)cobalt(III) tetraphenylporphyrin can oxidize allyl bromide in minutes. This pentacoordinated (nitro)cobalt(III) with enhanced activity is more easily generated using weaker Lewis base pyridines such as 3,5-dichloropyridine. Mechanistic studies indicate that the oxo transfer process involves both radical and nonradical pathways.[190]

A supramolecular structure in which a manganese porphyrin having two peripheral pyridine rings spontaneously assembles inside a large cavity formed by four zinc porphyrins tied together by chlorotricarbonylrhenium has been reported to act as epoxidation catalyst.[191,192] The system behaves like an artificial enzyme since a catalytically active metalloporphyrin is encapsulated inside a cavity that protects the active center and defines the size and shape of the accessible reagents. The manganese porphyrin increases its lifetime under reaction conditions from 10 min for the same bare complex to more than 3 h upon encapsulation. Pure manganese porphyrin loses its activity after 50 cycles, but the supramolecular structure reaches turnover numbers as high as 21 000. The selectivity of the catalyst can be tuned by adding up to two ligands which change the size of the cavity, allowing significant differentiation between substrates.[191] These results nicely illustrate how the stability and selectivity of metallo complexes can be increased by incorporation into a well-defined supramolecular structure.



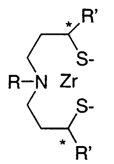
The same authors had previously reported that several manganese(III) porphyrins show significantly increased turnover numbers for the catalytic epoxidation of styrene upon addition of zinc and magnesium tetraphenylporphyrins.[193−195] For manganese porphyrin bearing two pyridyl substituents, 2−4-fold enhancement of the catalytic activity was measured. As in the case commented on earlier for the superstructure of manganese porphyrin encapsulated in the cavity defined by zinc porphyrins, this increase in the catalytic activity was attributed to the formation of a coordination trimer (metal ion other than manganese coordinated to the two peripheral pyridyl groups). This trimer would provide steric protection to the active oxomanganate intermediate avoiding bimolecular decomposition. In agreement with this hypothesis, in the absence of coordinating pyridyl moieties on the manganese porphyrin, less significant enhancement is observed.[193]

The redox potentials for reversible oxidation to the corresponding oxovanadium(V) cations (0.35 V vs SCE in dichloromethane) and irreversible reduction waves (in the range of −1.9 to 2.1 V vs SCE) have been measured by means of cyclic voltammetry for the oxovanadium(IV) complex of substituted dibenzotetraaza[14]annulene ligands.[196] From a preparative point of view, the oxovanadium(V) complex can also be obtained by oxidation of the oxovanadium(IV) complex with ferricenium hexafluoroantimonate, while unstable anionic oxovanadium(IV) complex was obtained by reducing the complex with sodium/potassium metal alloys.[196]



vanadyl complex of
dibenzotetraaza[14]annulene

Zirconium complexes of chiral aminodithiolate ligands act as catalyst for the enantioselective oxidation of geraniol with TBHP with 46% ee.[197] The same complex exhibits also Lewis acidity in the nitroaldol reaction with modest 30% enantioselectivity.[197]



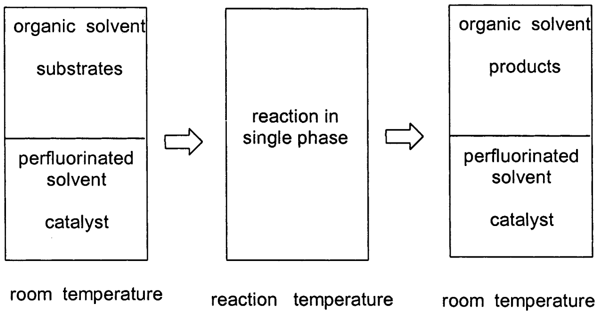
Chiral Zr complex

The above examples show that transition metal salts and their complexes are Lewis acids that can act as highly active and selective oxidation catalysts through formation of acid−base adducts.

### *2. Oxidations in Biphasic Fluorous Systems*

In the direction of development of catalytic oxidations in which the catalyst can be recovered and reused, one strategy is to use two immiscible liquid phases. An example of this approach is the biphasic fluorous system.

**Scheme 20**



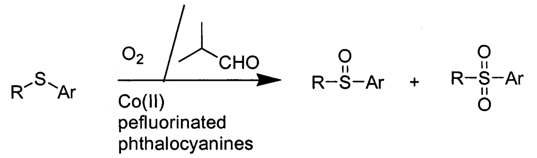
In the biphasic fluorous system, there is a perfluorinated organic solvent such as perfluoroalkanes that is not miscible at ambient temperature with most frequent organic solvents such as alkanes, ethers, or alcohols.[198−205] Upon heating of the sample at the reaction temperature, the system becomes homogeneous since miscibility of the two liquids increases considerably. Once the reaction has taken place, upon cooling the two liquid phases separate again, the catalyst remaining dissolved in the fluorous phase and the nonfluorinated solvent containing the reaction mixture. Scheme 20 summarizes the successive steps in a catalytic reaction based on fluorous system.

Besides the temperature-dependent miscibility of the two solvents, the key point of this strategy resides in the fact that the catalyst has to be very soluble in the perfluorinated solvent while the products are not. Since perfluorinated liquids are bad solvents (particularly compared with the polychlorinated analogues), the reaction products are generally not soluble in the perfluorinated liquid, but the first condition (exclusive solubility of the catalyst in the fluorous phase) normally requires the adequate functionalization of the catalyst. In this functionalization, a perfluorinated skeleton or perfluorinated tag is introduced in the molecule. This is normally accomplished through extensive and dedicated synthesis of the catalyst. This synthetic work and the limited number of catalysts that are suitable to be modified by introducing fluorinated “pony” tails constitute the main drawbacks of the biphasic fluorous strategy. In addition, the fluorinated solvents are very expensive and their availability at industrial scale is limited.

Biphasic fluorous systems have been widely used to effect oxidation reactions. Molecular oxygen is the oxidant of choice in most of the reported examples, although ozone can be used equally well.[206,207] This is mainly due to the high solubility of molecular oxygen in perfluorohydrocarbons. This makes oxidation processes in fluorinated solvents very attractive in terms of the use of oxygen as terminal oxidant and the possibility of catalyst recycle.[208] Several oxidation types including epoxidations, alcohol oxidation, and Baeyer−Villiger reactions have been carried out in fluorous solvents.

Readily available *n*-butyl 2,4-di(*n*-perfluorooctyl)phenyl selenide catalyzes the epoxidation of various olefins with $H_2O_2$ in a fluorous biphasic system.[209] The catalyst is selectively soluble in perfluorinated solvents, and can easily be separated, recovered, and

**Scheme 21**



reused several times without noticeable decrease in the final yield.[209] Alkenes can also be transformed into the corresponding ketones using TBHP in the presence of Pd(II) having perfluorinated ligands using benzene and bromoperfluorooctane as biphasic system.[210] Chiral (salen)manganese(III) complexes have been employed for the asymmetric epoxidation of indene with enantiomeric excesses up to 90%.[211] Compared to the use of oxygen as oxidant on biphasic fluorous systems, it seems that $H_2O_2$ or alkyl hydroperoxides are less advantageous.

$Pd(OAc)_2$ catalyzes the aerobic oxidation of alcohols into aldehydes and ketones in the presence of catalytic amounts of novel perfluoralkylated pyridine as ligand in a biphasic fluorous system composed of toluene and perfluorodecalin.[212] The fluorous phase containing the active Pd species is easily separated and can be reused several times without loss of activity. This catalytic system is applicable to benzylic and aliphatic alcohols.[212] A catalytic system containing 4,4′-bis(perfluorooctyl)-2,2′-bipyridine (2 mol %), $CuBr_2$-$(CH_3)_2S$ (2 mol %) and TEMPO (3.5 mol %) has been also reported to oxidize alcohols to aldehydes and ketones in a biphasic fluorous system of chlorobenzene and perfluorooctane directly with $O_2$.[213] The catalytic mixture can be reused four consecutive runs without observable loss in activity.

Cobalt(II) complexes of perfluorinated porphyrins and phthalocyanines have been used as catalysts for the oxidation of alkyl aryl sulfides with pivaldehyde/$O_2$ in biphasic fluorous systems (Scheme 21).[214] Sulfoxide is preferentially formed, together with variable quantities of sulfone. Cobalt perfluorophthalocyanines were found less efficient in terms of substrate conversion, but afford sulfoxides selectively.[214] The recycling of the catalyst was partly ineffectual owing to their partial degradation, particularly in the case of phthalocyanine complexes.

It is obvious that biphasic fluorous systems are interesting since they allow recycling and reuse of the catalyst. However, the major drawback is the need of dedicated synthetic efforts to make the catalysts soluble in perfluorinated solvents. The use of these expensive fluorinated solvents is also a limitation, particularly for large scale applications.

### *3. Heteropolyacids as Oxidation Catalysts*

Polyoxometalates and heteropolyacids are obtained by the condensation of two or more different types of oxoanions (eq 2). In these compounds, the anion contains a central atom, typically Si or P, tetrahedrically coordinated to oxygens and surrounded by 2−18 oxygen-linked hexavalent peripheral transition metals.[215−220] These are usually Mo or W, but it can also be others, such as Nb, Ta, U, either single or in combination. The most common structure in catalysis is the Keggin type heteropolyacid $(XM_{12}O_{40})^{n-}$, one specific example being the 12-tungstophosphoric acid.

$$12WO_4^{2-} + HPO_4^{2-} + 23H^+ \rightarrow PW_{12}O_{40}^{3-} + 12H_2O \quad (2)$$

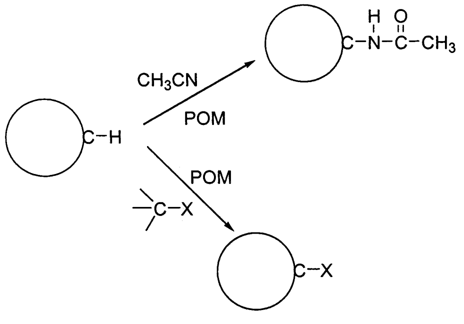
Heteropolyacids are mainly Brönsted acids. Given the large size of the polyanion having a low charge density delocalized through the surface, the interaction between the polyoxometalate anion and the compensating proton is weak and consequently they are strongly acidic. However, the interconversion between two oxidation states of the transition metal atoms or Lewis acid interaction renders these molecules or corresponding anions also oxidation catalysts.

Product distribution (propene or acetone) upon 2-propanol adsorption and FT-IR spectroscopy of adsorbed pyridine has been proposed as a test reaction to titrate the Brönsted and Lewis acid sites of commercial phosphomolybdic acid (Brönsted plus Lewis sites) or *n*-hexylammonium phosphomolybdate (exclusively Lewis sites) supported on silica.[221] Preferential propene formation over acetone, i.e., larger dehydration selectivity versus dehydrogenation, indicates a stronger surface acidity.

Polyoxometalates and phosphotungstates have been reported to act as catalysts for the direct formation of *N*-alkylacetamides and alkyl halides from adamantane, cyclohexane, and cyclooctane by reactiving them in acetonitrile or in halogenated solvents, respectively (Scheme 22).[222] It has also been found active to effect the catalytic conversion of highly toxic mustard gas bis(2-chloroethyl)sulfide into the nontoxic sulfoxides using TBHP in the presence of polyoxovanadate as catalyst.[223]

The oxidation of isobutane to methacrolein and methacrylic acid has been carried out over potassium/ammonium salts of phosphomolybdic acid of the Keggin-type with an overall selectivity to the desired products higher than 50%.[224] The presence of iron in the heteropolyacid composition led to a substantial enhancement of the catalytic activity with an increase of the desired products, even though the selectivity decreased.[224] Also pyridine treatment at 420 °C under $N_2$ flow promotes an enhanced catalytic activity for isobutane and propane oxidation with molecular oxygen to methacrylic and acrylic acids, respectively.[225] The deeper the pyridine treatment is,

**Scheme 22**



POM: Polyoxometallate

the higher the oxidation activity and selectivity to partial oxidation products. FTIR reveals that pyridinium ions remain adsorbed in the lattice of heat-treated $H_3PMo_{12}O_{40}$/pyridine, while on the surface Lewis acid sites are created due to oxygen vacancy defects in the Keggin structure.[225] On the basis of the above findings, it is proposed that the mechanism of alkane oxidation over $H_3PMo_{12}O_{40}$ involves acidity and electrons to activate $O_2$.

In an attempt to render the catalytic oxidations with polyoxometalates heterogeneous, these compounds have been supported on large surface area inorganic oxides.

Oxidation of propene to acetone has been studied over silica and alumina supported molybdophosphoric acid catalysts at 190 °C in the presence of water.[226] This overall process can be taken as the coupling of propene hydration and the oxydehydrogenation of 2-propanol, and, thus, the active catalysts must combine both acid and redox sites.[226] FT-Raman characterization of the catalysts shows that molybdophosphoric acid adsorbed on $SiO_2$ retains its Keggin structure while when supported on alumina it decomposes to $MoO_3$. $H_3PMo_{12}O_{40}/SiO_2$ showed almost no activity, while $MoO_3/Al_2O_3$ exhibits fairly good activity despite the stronger acid sites of the former. From this study, it was concluded that the rate-limiting step should be hydrogen abstraction on isopropoxy groups adsorbed on the catalyst surface.[226]

Heteropolytungstates have been immobilized by anion exchange with quaternary ammonium modified silica [227] and polysiloxane [228] or Amberlite IRA-900 resins.[229] Unfortunately, leaching of metal occurs, diminishing the interest of these electrostatically immobilized polyoxometales as heterogeneous oxidation catalysts.

Heteropolyacids having a defect structure incorporating a transition metal can catalyze the oxidation of alkylaromatics with molecular oxygen to aromatic carboxylic acids in acid media.[230] Analogously, oxidation of alkylarenes to the corresponding carboxylic acids or aromatic aldehydes by oxygen can be performed using a mixture of heteropolyacid and a transition metal complex dissolved in water.[231] Thus, a mixture of ruthenium acetylacetonate and phosphotungstic acid is effective for the oxidation of *p*-xylene with oxygen (60 kg $m^2$) at 200 °C in an autoclave.[231]

The decomposition of cumene peroxide into phenol and acetone, a process of paramount industrial importance, has been reported to proceed at temperatures between 30 and 60 °C in a batchwise procedure over supported heteropolyacid catalysts. The support for this process is a montmorillonite previously activated by $H_2SO_4$ treatment or metal ion (Zn, Fe, La, and Ce) impregnation.[232] Dodecatungstophosphoric acid exhibits 100% conversion within 5 min at 30 °C with complete selectivity. Correlation of the catalytic activity with acidity has revealed that both Lewis and Brönsted acid sites promote efficiently the decomposition.

As it will also be commented on later in the section devoted to permanganate, the pulp and paper industry is one of the industrial processes that consumes higher amounts of oxidants. A method to effect the oxidative degradation of soluble lignin and polysaccharide fragments dissolved during polyoxometalate delignification of pulps and fibers with oxygen has been reported.[233−235] This procedure to degrade oxidatively soluble lignin to volatile organic compounds can be catalyzed by a series of polyoxometalates of different compositions and stoichiometry, an example being $H_5(PV_2Mo_{10}O_{40})$.[234] It has been found that during the process the polyoxometalate undergoes a one-electron reduction by the electron-rich phenolic residues of lignin, which degrade through a consecutive series of sequential single-electron oxidations, first to cyclohexadienyl radicals and subsequently to cyclohexadienyl cations. The latter cationic intermediates would degrade by lateral chain cleavage.[236] The catalytic cycle is closed upon reoxidation of the reduced polyoxometalate form by oxygen.

Laser excitation of solid catalysts in the near-IR region can stimulate methane partial oxidation.[237] On the solid surface of $PW_{12}O_{40}{}^{3-}$ heteropolyanions, there exist Lewis basic sites located at W=O and W−O−W oxygens as well as Lewis acid sites at $W^{6+}$ cations. Methane is adsorbed by interacting with the Lewis basic sites, preferentially with W=O groups. Laser excitation at 980 $cm^{-1}$ of the W=O groups stimulates the oxidation of methane to methanol at temperatures higher than 100 °C. Other byproducts such as formaldehyde, dimethyl ether, and hydrocarbons are secondary products derived from primary methanol.[237]

As we have seen in the case of polyoxometalates, a widely used methodology to recover the catalyst is support the soluble Lewis acids onto an insoluble solid. In the next section, we will comment in detail on examples of this simple approach in the way towards isotropic (same composition and properties along the whole particle) solid catalysts.

### *4. Heterogeneized Homogeneous Lewis Acids as Oxidation Catalysts*

**a. Transition Metals Exchanged or Supported on Solids as Oxidation Catalysts.** In many oxidation processes in liquid phase, homogeneous catalysts in the form of oxometallic soluble complexes are used. However, these catalysts may present some limitations derived from the tendency of oxometallic species to oligomerize forming $\mu$-oxo complexes catalytically inactive, and also from the oxidative destruction of the ligands of the complex.

It appears that from the catalyst recovering point of view as well as for increasing the catalyst stability, it would be convenient to isolate and stabilize the metallic species by incorporating them into inorganic matrices and producing heterogeneous solid catalysts for liquid phase oxidations. This can be done by impregnating the active species on inorganic carriers, by anchoring one of the ligands of a transition metal complex on inorganic or organic carrier, by including "ship in a bottle" the metal complex within the cavities of a micro or mesoporous molecular sieve, by exchanging the Lewis acid in zeolites, and finally by synthesizing molecular sieves with framework Lewis acids able to carry out oxidation reactions.

Zeolites are crystalline aluminosilicates whose lattice consists of a network of $SiO_4^{4-}$ and $AlO_4^{5-}$ tetrahedra with Si or Al atoms at the centers and oxygen atoms in each corner.[238-242] The tetrahedra share the corners or edges; thus, the number of oxygens is twice that of Si plus Al atoms. In contrast to amorphous silica or silica−alumina, which lack long-range ordering, zeolites are crystalline; their tetrahedra are spatially arranged in strictly regular fashion.

A network of $SiO_4^{4-}$ tetrahedra is neutral; each $AlO_4^{5-}$ tetrahedron introduces one negative charge in the lattice. The negative charges are balanced by an appropriate number of cations, usually mono- or dipositive, inorganic or organic. Typical cations include alkali metal and quaternary ammonium ions. Since the chemical bonds between the crystalline framework and the cations are ionic, it is possible to exchange the cations partially or completely for different ones without modification of the rigid lattice.[243] The cations occupy empty space within the zeolites, in close proximity to the negative charges.

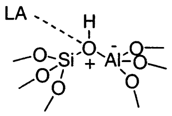
Concerning the chemical composition of the framework, the most important parameter is the Si/Al ratio. It may vary from Si/Al = 1 (faujasite X) to Si/Al = ∞ (silicalite). The Al or any other $T^{III}$ atom content of the silicate determines the number of cations in the framework, as well as other properties such as the thermal and chemical stability or the polarity of the internal surfaces. Typically, zeolites with a high Al content (X zeolite) are thermally and chemically less stable. In such cases, dehydration at high temperature may cause partial dealumination by the water being desorbed with a decrease of crystallinity ("self-steaming").[244] The chemical composition of synthetic zeolites can be controlled at two different stages: during the synthesis by varying the composition of the gels, or by postsynthetic modifications of as-synthesized samples.

Concerning the crystal structure of zeolites, the long-range ordering of the primary tetrahedra defines nondeformable channels and cavities of strictly uniform dimensions on the molecular scale (nanometer dimensions).[245,246] This porosity explains why the surface area per unit weight of zeolites is among the highest for any solid. The total surface area of zeolites is the sum of the external and internal surfaces.

Brönsted acid sites in zeolites are due to hydroxyl groups bridging a Si and Al atom.[247-249] The $H^+$ forms of zeolites can be prepared from alkali ion containing forms by ion exchange with concentrated hydrochloric acid at elevated temperatures. This procedure usually results in partial dealumination, causing damage to the crystalline structure. A milder dealumination method implies the exchange of alkali ions by $NH_4^+$, and subsequent thermal decomposition eliminates $NH_3$, leaving $H^+$ in the framework. Likewise, calcination of as-synthesized zeolites containing quaternary ammonium ions generates a proton in the lattice. The protons of acidic zeolites are not free, but covalently bonded to the oxygen closest to a negatively charged aluminum, forming oxonium species. The bridging ≡Si−(OH)-Al≡ hydroxy groups can be monitored by IR spectroscopy.

Zeolites may contain Lewis sites in addition to Brönsted sites.[247] These sites can be attributed to tricoordinated or partially dislodged Al centers. However, this type of Al has resisted detection by $^{27}Al$ MAS NMR. On the other hand, samples exhibiting Lewis acidity have octahedrally coordinated Al extraframework species, and these extraframework Al species (EFAL) show Lewis acidity. EFAL centers are generated during steaming or calcination of hydrated zeolites, especially of the $NH_4^+$ or $H^+$ forms. EFAL not only generates Lewis sites, but also reduces the population of Brönsted centers. Two types of EFALs can be distinguished. Mild steaming conditions favor low-weight oligomers of cationic polyoxoaluminate EFAL species, which can be removed by treatment with oxalic acid or $(NH_4)_2SiF_6$,[240] whereas more drastic steaming conditions lead to highly condensed (polymeric) EFAL, that cannot be dissolved by $(NH_4)_2SiF_6$.

Finally, the interaction with EFAL Lewis sites is expected to enhance the strength of Brönsted sites also present.[250,251] The enhancement of Brönsted acidity by Lewis sites has also been invoked in other cases to explain the superacidity of sulfated zirconia and related transition metal superacidic oxides.[250,251]



Lewis acid (LA) enhanced Brönsted acidity

In the case of zeolites, transition metal elements can be introduced in different structures, different oxidation states, and coordinations, either as extraframework exchanged cations, supported metal clusters, supported metal oxides, complexes or as lattice cations. These transition metals present in the composition of the zeolite will be responsible for the activity of the zeolite as catalysts in oxidation reactions.

For instance, $Mn^{2+}$, $Ni^{2+}$, and $Co^{2+}$ ion exchanged X zeolite is able to oxidize *n*-hexane with $O_2$ in liquid phase to yield 70 to 80% selectivity to acetic acid. The fact that the rate of formation of acetic acid is the same for the metal exchanged zeolites than for the homogeneous reaction with those metals, may indicate not only that the metals leach out of the zeolite but also that the leached metals play a determinant role in the observed activity.

Methane is an abundant hydrocarbon, and new processes to effect its partial oxidation are desirable. In this context, it has been found that water has a detrimental influence on the activity of In/HZSM-5 zeolite as catalyst for the selective oxidation of methane by nitric oxide. Apparently, water interacts with the Lewis acid sites of the zeolite and retards the transformation of NO into $NO_2$ an elementary step in the oxidation of methane by NO.[252] The co-incorporation of Pt, Rh, or Ir to the In/HZSM-5 zeolite renders the catalyst more tolerant to the presence of water vapor.

Chromium oxide supported on mesoporous MCM-41 as well as Zr- or La-doped silica has been found to be an active catalyst for the dehydrogenation of propane at temperatures between 350 and 550 °C. The partial substitution of Cr(III) ions by Al(III) increases the Brönsted and Lewis acidity and favors the selectivity to propene.[253] On the other hand, substitution of Cr(III) by Ga increases the number of Lewis acid sites and the oxidizing power of the solid.[253]

Ethylene and propylene have been oxidized using transition metals on zeolites. For instance, ethylene is selectively oxidized to ethylene oxide on $Ag^+$ impregnated on zeolites, but selectivity is low on $Ag^+$ exchanged zeolites.[254] Propylene dissolved in benzene was oxidized with $O_2$ at 150 °C and 45 bar on molybdenum impregnated X zeolite with high selectivities to the epoxide. However, for conversions above 5% further oxidation of the epoxide occurs with formation of methanol, formic and acetic acid as well as esters of the epoxide and the above acids.[255] Propylene can be oxidized to acetone by Mo or Pd/Cu exchanged Y zeolites.[256−260] With the Pd/Cu catalyst the active component for olefin oxidation is $Pd^{2+}$, and $Cu^{2+}$ is used as a promoter for the reoxidation of $Pd^0$.

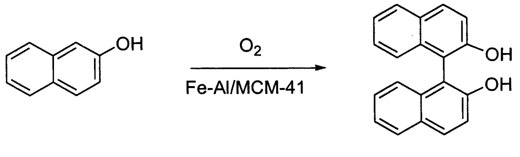
Dealuminated Y zeolites were used to encapsulate $Mo(CO)_6$.[261] Subsequent decarbonylation renders a solid that can act as catalyst in ammonia decomposition. The oxidation state of molybdenum and the overall acidity of the material correlates with its catalytic activity toward ammonia decomposition.[261]

Transition metals such as copper and iron can be introduced in MCM-41 by ion exchange. Even *all-silica* MCM-41 that has no charge-balancing cations can admit substantial amounts of iron ions from a methanolic solution. These mesoporous MCM-41 containing $Cu^{2+}$ or $Fe^{3+}$ can act as *redox* catalysts and can convert $N_2O$ into NO at room temperature.[262]

$Fe^{3+}$- and $Cu^{2+}$- exchanged Al/MCM-41 have been found convenient catalysts for the oxidative coupling of 2-naphthol by oxygen or air to form 1,1′-binaphthyl (Scheme 23).[263] High conversion and good selectivities have been achieved using Fe-Al/MCM-41.[263] This coupling can also be performed using $FeCl_3/SiO_2$, $FeCl_3/Al_2O_3$, $Fe^{3+}$-exchanged montmorillonite, and $Fe^{3+}$ and $Cu^{2+}$ exchanged Y zeolite.[264] In the latter case, a large fraction of the product formed inside the zeolite cavities cannot diffuse out and remains trapped due to the large molecular size of binaphthyl compared to the windows of Y zeolite (0.74 nm).

Highly dispersed transition metal oxides were obtained by ion-exchanging commercial NaY zeolite with the corresponding salts of transition metal and treating them with NaOH. The resulting zeolites containing encapsulated transition metal oxides, particularly the cobalt oxide@Y, were found to be active to effect the complete oxidation of air-diluted toluene.[265]

**Scheme 23**



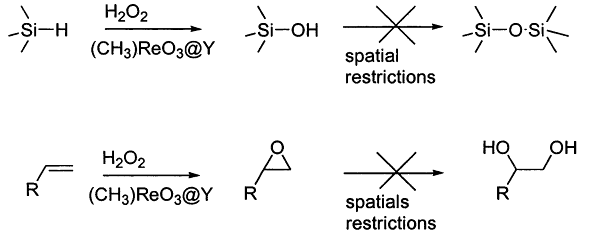
**b. Encapsulated Transition Metals as Oxidation Catalysts.** One of the simplest strategy to convert an homogeneous into heterogeneous catalyst is by supporting it by impregnation on a solid.[266] This leads to catalysts that very easily leach the active species in solution, and therefore this method has limited interest unless it is demonstrated beyond any doubt that no migration of the active sites to the liquid phase occurs during extensive use of the catalyst. A procedure for avoiding leaching or, at least, for strongly reducing the process, will be to encapsulate the active bulky species within the cavities of zeolites.

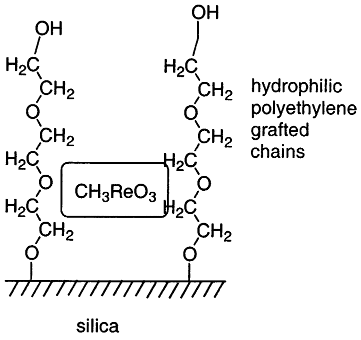
A step forward in the application of Lewis acids for oxidation process, involves the encapsulation of methyltrioxorhenium or tungstates and heteropolytungstates using $H_2O_2$ as oxidant. Both types of catalysts have shown to be effective for epoxidation with $H_2O_2$ in homogeneous phase.[156,267,268] Thus, methyltrioxorhenium has been adsorbed within the supercages of zeolite NaY and used as heterogeneous catalysts for the oxidation of silanes to silanols and epoxidation of olefins using hydrogen peroxide (Scheme 24).[269] Both reaction types proceed with high conversions and selectivities using the encapsulated organometallic compound. In particular, the formation of disiloxanes in one case or the vic-diols in the other, being two processes normally occurring using the homogeneous $MeReO_3$ catalyst, are not observed using encapsulated $MeReO_3$@NaY. These two undesired processes occur from the adventitious Lewis acid-catalyzed condensation of two silanols or from the acid-catalyzed epoxide ring aperture. The high selectivity of the oxidation of $MeReO_3$@NaY was interpreted as due to the spatial restrictions imposed by the zeolite lattice to the occurrence of bimolecular reactions.

One problem encountered in the oxidation of hydrocarbons with hydrogen peroxide is the inmiscibility of both type of liquids and the difficulty of having an appreciable concentration of substrate and oxidant at the catalytic center. To overcome this problem, an elegant strategy has been to attach covalently poly(ethylene oxide) and poly(propylene oxide) chains to the surface of the silica particles containing methyltrioxorhenium.[270] The presence of these polymeric chains greatly increases the miscibility of the two liquid phases on the catalyst surface. The resulting solid efficiently catalyzes the epoxidation of alkenes with hydrogen peroxide.

The influence of encapsulation inside the pores of zeolite on the activity and selectivity of incorporated guest can be exemplified by the case of mixed iron−molybdenum oxides encapsulated in boralite (FeMo/

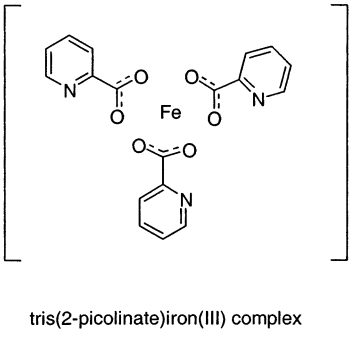
**Scheme 24**





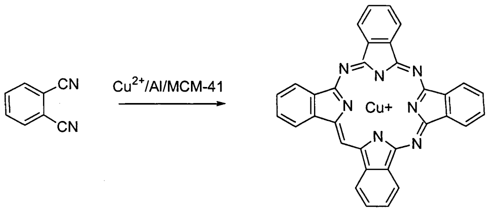
Bor). For the selective oxidation of toluene to benzaldehyde, the activity and selectivity of FeMo/Bor have been compared with that of two other conventional catalysts for this process such as vanadium oxide supported on titania and bulk $Fe_2(MoO_4)_3$.[271] $V/TiO_2$ exhibits a pronounced decrease in the selectivity toward benzaldehyde at increasing toluene conversions compared to FeMo/Bor. This effect was attributed to the presence of stronger Lewis acid sites in $V/TiO_2$ which activate the C═O group facilitating its further oxidation to benzoate derivatives. On the other hand, FeMo/Bor shows higher selectivity than $Fe_2(MoO_4)_3$ at low toluene conversions due to the spatial constraints to the catalytic activity of the mixed Fe–Mo by the zeolite channels, but lower selectivity at high conversions. In the latter case, the longer residence time due to diffusion limitations inside the zeolite channels facilitates the occurrence of secondary reactions in which the aromatic ring undergoes further oxidation to form maleic anhydride and carbon oxides.[271]

In an extensive series of articles, Barton and coworkers have developed and optimized different catalytic systems, commonly termed as Gif systems, to perform the oxidation of alkanes with hydrogen peroxide or organic hydroperoxides in solution.[272–280] One of the most convenient systems uses the complex of $Fe^{3+}$ and picolinic acid working in a mixture of acetonitrile–pyridine as solvent and hydrogen peroxide as oxidant.[276,277] A heterogeneous version of this reaction has been reported in which the $Fe^{3+}$-picolinate complex has been assembled inside the pores of $Fe^{3+}$-exchanged zeolites by subsequent addition of picolinic acid.[281] The complex remains immobilized inside the zeolite cavities and channels. This encapsulated complex can catalyze the oxidation of cyclohexane with 93% hydrogen peroxide selectivity toward oxidation at 49% cyclohexane conversion and >90% cyclohexanone selectivity.[281]

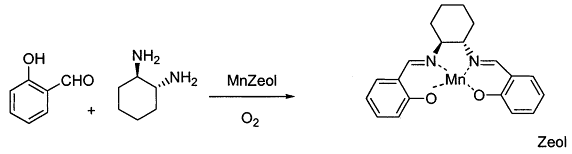


tris(2-picolinate)iron(III) complex

**Scheme 25**



**Scheme 26**



$Cu^{2+}$-phthalocyanine and $Co^{2+}$-perfluorophthalocyanine have been prepared inside the pores of MCM-41 by heating a mixture of *o*-dicyanobenzene and $Cu^{2+}$ or $Co^{2+}$-exchanged MCM-41 at 200 °C under reduced pressure for 24 h (Scheme 25).[282] The resulting solids supporting metal phthalocyanines have been tested as catalyst for cyclohexane oxidation with hydrogen peroxide or TBHP. The latter was found a more convenient oxidizing reagent. $Co^{2+}$perfluorophthalocyanine supported on MCM-41 was found more active than the same unsupported complex or when encapsulated in zeolite Y. However, the selectivity of the oxidant toward oxidation of cyclohexane was only moderate.[282]

One remarkable example of an encapsulated transition metal complex is the case of chiral Mn(III) salen complex entrapped within the cages of zeolites Y and EMT.[283,284] The complex was prepared by performing the ship-in-a-bottle synthesis of the salen ligand derived from 1,2-diaminocyclohexane around resident Mn(II) ions (Scheme 26). These solids were active for the asymmetric epoxidation of aryl olefins with iodosylbenzene. The highest enantiomeric excesses achieved with the encapsulated complex (~60%) were, however, significantly lower than those achieved for the same complex in homogeneous phase (>90% ee).[179]

**c. Transition Metal Lewis Acids Grafted on Solids.** In general, it has to be remarked that metals either exchanged or impregnated in zeolites can leach when operated in liquid phase processes, especially if polar reactants or products are involved. This will also apply to supported metal oxides on other carriers. However, special mention should be made to the Shell catalyst[285] that consists of titanium covalently grafted on silica ($Ti/SiO_2$). This is a real heterogeneous oxidation catalyst that works in liquid phase, but which is only active with organic peroxides. The catalyst containing between 1 and 2.5 wt % of $TiO_2$ on silica is prepared by impregnating silica (high surface fume silica) with a Ti(IV) precursor that affords after activation Ti–O- grafted on the surface silanols of the support. $TiCl_4$ and Ti(O-i-Pr)$_4$ are good precursors that leave Ti(IV) attached to the surface by at least three silanol groups.[286–288] It has been shown that a Si–Ti (O-i-Pr) catalyst treated with tartaric acid was active for epoxidations with 30% $H_2O_2$ at 80 °C with reactive olefins such as cyclooctene or cyclohexene. The last cycloalkene gives mixtures of epoxide, cyclohexane-1,2-diol, and allylic oxidation products. Ti(IV)/$SiO_2$ Shell type catalyst offers an alternative to ARCO's technology (oxirane process) for the production of epoxides and more specifically propylene epoxide using an alkyl hydroperoxide. ARCO's process uses a homogeneous catalyst based on Mo. The reaction proceeds via a peroxometal pathway, and the active catalyst contains the metal in its highest oxidation state. Metals with low oxidation potential and high Lewis acidity in their highest oxidation states are superior catalysts and show the order of reactivity Mo(VI) > W(VI) > V(V) > Ti(IV).[289] The activity of these homogeneous catalysts is strongly diminished by the presence of polar molecules such as $H_2O$, alcohols, and especially glycols that can strongly coordinate with the metal. The epoxidation is stereospecific, i.e., cis olefins give only cis epoxides, and the rate increases with increasing the electron density at the C=C double bond, i.e., with increasing the substitution of the double bond by electron donating alkyl groups. This effect is consistent with a nonradical mechanism involving an electrophilic oxidant.[290]

The development by Shell of the heterogeneous silica-supported titania catalyst described before was an important step toward an environmentally benign catalyst. Commercially, it is applied to the epoxidation of propylene with ethylbenzene hydroperoxide. The alcohol coproduct is dehydrated in a separate stage to styrene. The higher catalytic activity of Ti(IV)/$SiO_2$ with respect to soluble Ti(IV) was attributed to the site isolation and fixation of Ti(IV) on the surface that prevents oligomerization to unreactive $\mu$-oxo species. Formation of these $\mu$-oxo species readily occurs with soluble Ti(IV) catalyst.[291] It also appears that the Lewis acidity of Ti(IV) is increased when on silica due to electron withdrawing by silanoxy ligands. Unfortunately, the Ti/$SiO_2$ catalyst is deactivated by the presence of $H_2O$,[289] and consequently this catalyst is not efficient using $H_2O_2$ as oxidant. A similar problem arises from the amorphous titania–silica mixed oxides prepared by the solution sol–gel procedure. Acid-catalyzed hydrolysis and polycondensation of Ti- and Si-alkoxides gives amorphous mixed oxides with Ti contents much higher than the 2.5 wt % achieved in the Ti(IV) grafted silica. These materials prepared by the sol–gel procedure, when dried by extraction with supercritical $CO_2$, yields a mesoporous material with a very high surface area and isolated Ti(IV).[292] As described earlier for Shell catalysts, these materials are sensitive to water and are not suitable for working with $H_2O_2$, even when its hydrophobicity is increased.[293,294]

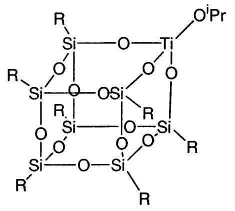
Mixed Ti/Si oxides have been analyzed by EXAFS. This study has revealed that, while octahedral Ti coordination predominates at high Ti percentages, the amount of tetrahedral Ti increases as the Ti content decreases reaching a maximum between 10 and 20 mol % of Ti.[295] Lewis acid measurements and catalytic activity for 1-octene epoxidation with TBHP indicate that these two features are due to tetrahedral Ti. It is proposed that the coordinative unsaturated tetrahedral Ti can expand its coordination sphere by interaction with a Lewis base or with the hydroperoxide.[295]

Comparison of the performance of unmodified and dimethylaminopropyl-modified $TiO_2/SiO_2$ aerogels for α-isophorone epoxidation with TBHP establishes that the amine group diminishes the epoxidation activity of $TiO_2/SiO_2$, but it also eliminates the activity in acid-catalyzed side reactions, such as epoxide ring aperture and peroxide decomposition.[296] It was found that addition of methanol to an unmodified $TiO_2/SiO_2$ has a similar effect. These observations suggest that the electron donation by the alkylamino groups or methanol to the Ti active site (Lewis acid) suppresses its acidity and, thus, inhibiting acid-catalyzed reactions. On the other hand, the surface Si–OH groups of $TiO_2/SiO_2$ have low activity for epoxide decomposition.[296]

### *5. Soluble Compounds as Models for the Active Sites in Solid Lewis Acid Oxidation Catalysts*

In the way to the development of solid catalysts and understanding of the nature of their active sites, a line of research consists of the preparation of soluble molecules or metal complexes with well-defined molecular structure that could serve as models for the sites present in the solid. Normally, a solid catalyst contains a distribution of different catalytic sites varying in the coordination sphere or in the location of the site in the solid. It is believed that the intrinsic catalytic activity of a given metal atom can be different from others depending on the actual structure. Therefore, the optimum solid catalyst should contain the maximum density of the most active metal atoms while being devoid of others with lower activity and selectivity.

An example of the previous strategy is the preparation of titanosilsesquioxanes with different structures to test their catalytic activity in the epoxidation of olefins.[297–299] As it will be commented, solid titanosilicates are widely used as solid catalysts for the epoxidation of alkenes, hydroxylation of aromatics, oxidation of alcohols and amines, etc. The question is which types of titanium atoms are the most active. One approach to address the specific activity of sites with different coordination around the titanium atoms consists of crossing the structural information from characterization techniques such as EXAFS and XANES obtained for a series of solids with the catalytic tests of the series. However, due to the current low resolution of solid characterization techniques, the degree of uncertainty of this approach is always higher than the use of molecular titanosilsesquioxanes having a structure analogous to that of a cluster of titanosilicate.



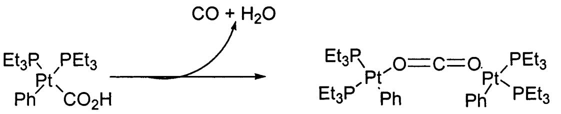
Titanosilsesquioxane

In the way to solid epoxidation catalysts titanosilsesquioxanes, that are excellent homogeneous catalysts for epoxidation of olefins using TBHP, have been heterogeneized by adsorbing them in the pores of MCM-41. Previously, the MCM-41 was modified by silylation with $Ph_2SiCl_2$ to passivate the external surface.[300] The supported titanosilsesquioxane is claimed to be a reusable catalyst for epoxidation with *tert*-butylhydroperoxide.

Likewise, the influence of the coordination sphere of each active titanium site in titanogermanosilicate solids has been addressed by preparing soluble titanogermanosilsesquioxane and determining separately the activity of each compound and the influence of the presence of germanium.[301]

Studying the specific reactivity of soluble complexes with different structures allows one to assess the intrinsic activity of each site. An additional refinement of this strategy is to prepare even the catalytically active oxo intermediate, such as the oxo complex. This allows the determination in homogeneous phase of the rate of elementary steps such as hydrogen abstraction or the transfer of an oxo group. An example of this approach has been the synthesis of a limited number of transition metal hydroxycarbonyls.[302−304] These metallic complexes are the reaction intermediates in various transition metal catalyzed reactions of CO and $H_2O$ including the oxidation of CO, the homogeneous water-gas shift, and the formation of metal hydrides. Although, as expected, $\beta$-elimination to give a metal hydride and $CO_2$ is the usual mode of decomposition, it was demonstrated that the ease of this process is metal- and ligand-dependent. For *trans*-$Pt(CO_2H)(C_6H_6)(PEt_3)_2$, an alternative route was identified in which CO and $H_2O$ are lost and a dinuclear complex having a bridging $CO_2$ is formed (Scheme 27).[305]

**Scheme 27**



Giving the potential of this methodology to understand the activity of solid catalysts, it can be anticipated that more effort would be dedicated to the synthesis of soluble mimics of solid active centers. This methodology relies on the fact that the reaction intermediates in solution are analogous to those present in the solids. However, immobilization of the active site may alter the reaction mechanism. Thus, the mechanism of the solution-phase homogeneous oxidation of pyrocatechol using cobalt or vanadium oxides was found to be different to that of the vapor-phase heterogeneous process.[306]

### 6. Transition Metal Lewis Acids in the Walls of Mesoporous Molecular Sieves

Mesoporous molecular sieves and more specifically Ti-MCM-41 were first synthesized in 1994.[307,308] This material with surface areas ≥ 800 $m^2\ g^{-1}$ showed the Ti to be tetrahedrally coordinated and isolated in the silica matrix.[309] The larger pore size of this mesoporous solid makes it more active as catalysts for reactions in which large substrates and reagents participate, even though its intrinsic activity measured for small reagents has been determined to be considerably lower than for TS-1 or Ti/Beta titanosilicates. Ti-MCM-41 was active and selective for carrying out the epoxidation of olefins with both TBHP and with $H_2O_2$, but the results were much better with TBHP. After this, other Ti-containing mesoporous molecular sieves such as HMS, MCM-48, MSU, UTD-1, and JDF-L1 have been synthesized.[308,310−314] These are hydrophilic materials that adsorb $H_2O$ and due to the Lewis acidity of the Ti atoms opens the epoxides giving thiols. These diols become strongly adsorbed on the Ti sites leading not only to a decrease of epoxide selectivity but also to a decrease in catalyst activity. A thorough study of catalyst synthesis together with postsynthesis treatments was carried out by Corma et al.[315,316] They showed that by optimizing the synthesis of Ti-MCM-41 in the absence of TMAOH, and by the proper silylation of the surface of the resulting material very active and extremely selective epoxidation catalysts could be produced when using either TBHP or cumene hydroperoxide as oxidizing agents, with feeds that contain even 2 wt % of $H_2O$ (Figure 1). These catalysts offer great promise for epoxidation of propylene using organic peroxides, owing to their extremely high selectivity to the epoxide and the very low formation of diols, that minimize deactivation and increase the catalyst life.

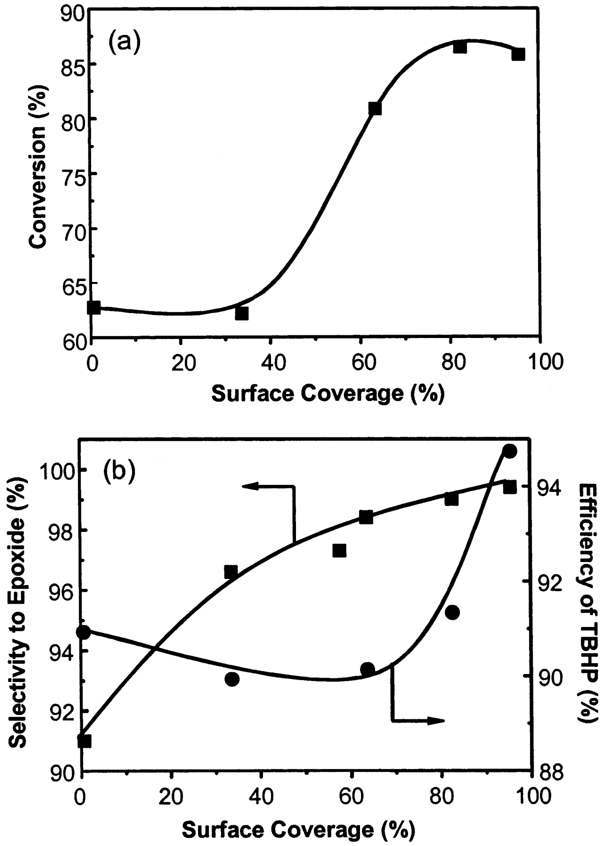


**Figure 1.** Influence of the silylation (as degree of surface coverage) of Ti/MCM-41 on the conversion (a) and selectivity (b) for the cyclohexene epoxidation with TBHP (Reprinted with permission from ref 315. Copyright 1998 Chemical Society London).

It has been reported that Ti/MCM-41 in which Lewis acid sites are also present can act as a bifunctional catalyst in the one-step conversion of α-pinene to campholenic aldehyde, promoting the epoxidation of the C=C double bond and the subsequent rearrangement of the resulting pinene epoxide with ring aperture.[317]

Mesoporous molecular sieves with transition metals other than Ti (Zr, V, Sn) have also been prepared. They are active for oxidation reactions with organic peroxides and $H_2O_2$, but the possibility of metal leaching should be carefully addressed in each case.[123,318−325]

Nb-containing MCM-41 has been modified with ammonium and copper cations and tested for several oxidation reactions including NO decomposition, selective oxidation of $NH_3$ by NO, hydrosulfurization of methanol, and oxidation of thioethers with hydrogen peroxide to sulfoxides.[326] The same Nb/MCM-41 solid after ion exchange with ammonium and dehydroxylation exhibits Lewis acidity and is able to catalyze the reaction of methanol with hydrogen sulfide to form methanethiol.[326] On the other hand, although $Cu^{2+}$ ions adsorbed on Nb/MCM-41 show a higher reducibility as compared with Al/MCM-41, this does not lead to a higher activity of Nb/MCM-41 for the catalytic NO decomposition.[326]

Vanadium-containing MCM-41 has equally been prepared and found to exhibit catalytic activity toward the gas-phase partial oxidation of methanol to formaldehyde.[327] The solid is stable under reaction conditions at 350 °C. The main active site is proposed to be isolated tetrahedral vanadium atoms coordinated to surrounding oxygen anions, which is the predominant site at vanadium percentages below 0.41 wt %.[327]

Enantioselective epoxidation of allylic alcohols using titanium complexes of diethyl tartrate[175−178,328] has been a significant achievement in asymmetric catalysis, that paved the way to enantioselective epoxidation in general. Some work has been carried out trying to obtain Ti-containing solids for the heterogeneous version of allylic alcohol epoxidation. Thus, epoxidation of allylic alcohols with TBHP can be catalyzed by titanium-containing pillared montmorillonites.[329] The pillars are polymeric Ti cations formed by partial hydrolysis of $TiCl_4$ with HCl. The interlayer distance, specific surface area, and thermal stability of the resulting pillared clay depend on the pH of the pillaring solution. For a $H^+$/Ti ratio of 0.24, the Ti-pillared clay shows a basal spacing of 2.6 nm, a specific surface area of 316 $m^2\ g^{-1}$ and does not collapse at temperatures below 500 °C.[329] This titanium-containing clay catalyzes the oxidation of (*E*)-2-hexen-1-ol with TBHP in the presence of diethyl tartrate with 50% yield, when it has been activated by calcining the solid in air at 500 °C and the reaction is conducted at 23 °C.[329] This yield is comparable to that reported for the same allylic alcohol using polymer supported Ti(IV) as catalyst.[329]

## *7. Transition Metal Lewis Acids in the Framework of Microporous Molecular Sieves*

**a. Ti−Silicalite.** An important breakthrough in the use of Lewis acids as heterogeneous environmentally friendly catalysts was the discovery of the activity of Ti-silicalite (TS-1) as a catalyst for a series of useful oxidation reactions using $H_2O_2$ as oxidant.[330−333] TS-1 is a zeolite with MFI structure whose topology is formed by a two-channel system with diameters 0.53 × 0.56 and 0.51 × 0.51 nm, respectively. Ti was incorporated in the framework of silicalite as isolated tetrahedral Ti(IV), and it appears that the site isolation resulting from the incorporation during the synthesis of the molecular sieves produces the most promising type of solid Lewis acids oxidation catalysts for liquid-phase operations. These Ti-containing silicalites should be, in principle, more stable toward leaching taking into account the lower accessibility of the Ti−O bonds. On top of this, Ti-zeolites have adsorption properties that can be tuned from the point of view of their hydrophobicity−hydrophilicity, allowing a certain control on the proportions of reactants with different polarities within the pores. Thus, owing to the silica framework with little number of defects, the TS-1 is a hydrophobic catalyst that can use $H_2O_2$ as oxidant. Using this environmentally friendly oxidant, reactions such as oxidation of alcohols, epoxidation of linear olefins, hydroxylation of aromatics, ammoximation of cyclohexanone, oxidation of alkanes to alcohols and ketones, oxidation of amines, oxidation of sulfur-containing compounds, and oxidation of ethers, among others, have been carried out selectively with TS-1.[114,334−340] A summary of the reactions catalyzed by TS-1 is given in Figure 2.

The proper design of TS-1 catalysts involves the introduction during the synthesis of Ti in framework positions. A necessary requirement for the successful synthesis of TS-1 is to carry it out in the absence of significant amounts of alkali metal ions to avoid the precipitation of alkali titanates during the synthesis.

Different synthesis routes have been proposed using various Si and Ti precursors, and several structure directing agents (SDA) and mineralizers. A summary of those is given in Figure 3.

Since the first moment, the exceptional oxidation properties of TS-1 were related to the presence of isolated tetrahedral Ti(IV) in framework positions, since silicalite was not active and $TiO_2$ (anatase) produced the decomposition of $H_2O_2$.[341] However, it is not easy to prove unequivocally the incorporation of Ti in framework positions since the low Ti contents (1−2 wt %) make impossible the determination by XRD. The importance of these catalysts has triggered a large effort on characterization, and a combination

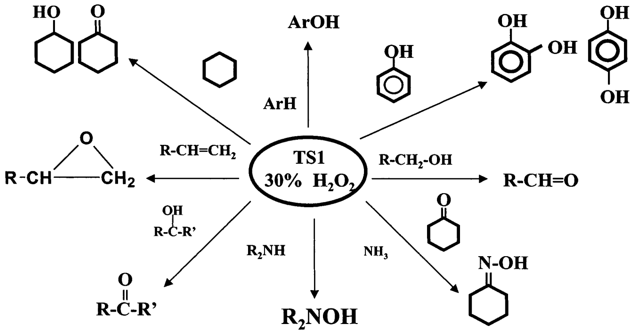


**Figure 2.** Oxidation reactions catalyzed by TS-1.

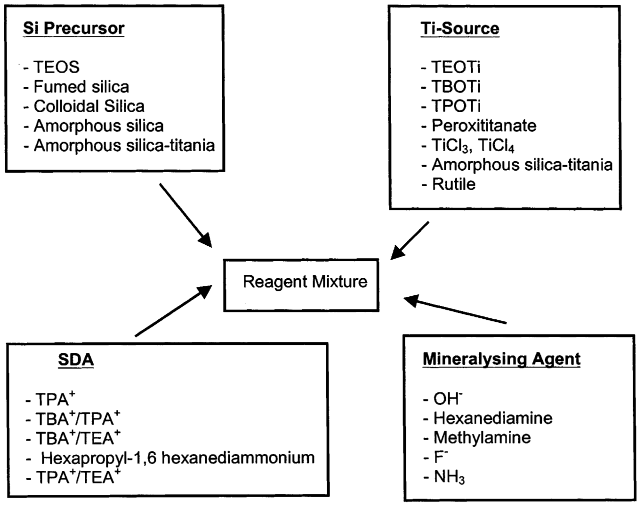
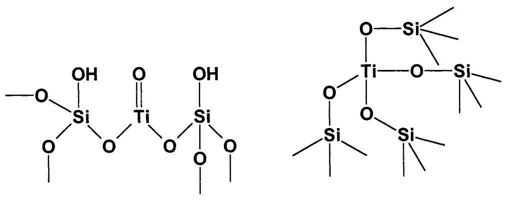


**Figure 3.** Summary of the synthetic procedures to obtain TS-1.

of XRD, IR, UV−Visible, XPS, and EXAFS/XANES spectroscopies have confirmed the presence and the amount of TI(IV) framework sites. A good review on this has been published recently.[342] More recently, electrochemical and photochemical techniques have also been used to address this issue.[343−345]

On the basis of the above characterization techniques, two structures differing in the presence of titanyl groups (Ti=O) or tetrahedral Ti have been proposed for the isolated Ti(IV) species (Scheme 28).

**Scheme 28**



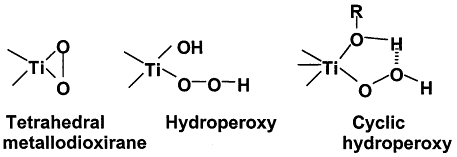
Proposed Structure with titanyl groups

Proposed Structure with tetrahedral Ti atoms

The presence of titanyl groups is consistent with the observation of a band at 960 $cm^{-1}$ in the IR spectrum of TS-1. However, other pieces of evidence do not confirm this assignment. For instance, the UV−Visible spectrum of TS-1 does not show a band between 25 000 and 35 000 $cm^{-1}$ characteristic of the Ti=O group. On the other hand, the position of the 960 $cm^{-1}$ IR band is not modified by $D_2O$ treatment, but it shifts to lower frequencies with the $H_2{}^{17}O$ exchange.[346] Furthermore, the intensity of this band is not affected by the treatment of the sample with $SO_2$.[14] Thus, even if it is now generally accepted that Ti is tetrahedrally coordinated with framework oxygens, Sinclair and Catlow do not rule out the formation of Ti=O groups under the reaction conditions.[347] These titanyl groups would be formed by hydrolysis of the Ti−O−Si bond in the presence of $H_2O$.

The geometry of the Ti centers has been successfully determined by means of UV−Visible and EXAFS/XANES spectroscopies. Indeed, the dehydrated TS-1 shows a UV−Visible band at 48 000 $cm^{-1}$, that is not present in silicalite, and which is associated to charge-transfer processes localized in isolated Ti atoms in tetrahedral coordination.[348] The presence of polymeric species of hexacoordinated Ti gives rise to an absorption band at 42 000 $cm^{-1}$, while anatase or rutile have absorption bands at 30000−35000 $cm^{-1}$.[349]

**Scheme 29**



The XANES spectrum of TS-1 and its comparison with other Ti compounds in which the coordination of Ti is well established has revealed the presence in dehydrated TS-1 samples of tetrahedrally coordinated Ti.[350,351]

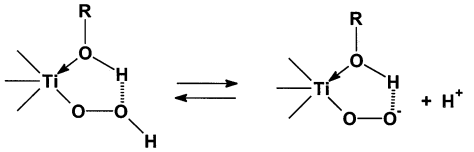
The incorporation of Ti in the MFI structure produces an expansion of the framework and an increase in the tension around the Ti center owing to the larger $[TiO_4]$ size compared to $[SiO_4]$ tetrahedra. The Ti(IV) can interact with $H_2O$ producing the hydrolysis of one or more Ti−O−Si bonds, which results in a local relaxation of the structure at the Ti sites. It is important to point out that for acting as a catalytic site, the Ti(IV) in TS-1 has to interact with reactants. Thus, to be able to increase its coordination number during the adsorption process, Ti should move from the original framework position to another more external and relaxed in which the Si−O−Ti bonds will be more polarized and elongated with respect to the normal values. The ability of Ti in TS-1 to increase the coordination sphere without becoming separated from the zeolite framework is a key point for the special catalytic properties of Ti in TS-1 and more generally Ti in zeolites.

Following the chemistry of the Ti(IV) complexes in liquid phase, $H_2O_2$ acts as a bidentate ligand ($\eta^2$-$O_2$) replacing other ligands to form very stable metallodioxirane or peroxo complexes (Scheme 29). The organic hydroperoxides form a peroxocomplex analogous to the hydroperoxy species shown in Scheme 29.

The interaction of $H_2O_2$ with the Ti centers of Ti-zeolites generates a UV−Visible band at 26 000 $cm^{-1}$ which has been assigned to a charge-transfer interaction between the hydroperoxide (OOH) ligand and Ti(IV).[352] Nevertheless, the $[Ti(O_2)F_5]^{3-}$ ion also shows an absorption band at ∼26 000 $cm^{-1}$ which can be associated to the $O_2{}^{2-} \rightarrow Ti^{4+}$ charge transfer. Thus, it becomes difficult to distinguish between hydroperoxy and titanodioxirane based on the UV−Visible spectra. Some authors have considered a tetrahedral metallodioxirane species as the reaction intermediate on TS-1 (Scheme 29). However, this species cannot explain the effect of acids, bases, and solvents on the reaction kinetics, nor the high activity of TS-1 with diluted solutions of $H_2O_2$ in protic media.[353]

Nevertheless, Talsi claims[354] that with the adequate ligands, the Ti peroxo complexes $(Ti(O_2)(OEt)_2L_2)$ can be active in oxidation reactions and the acid−base and solvent effects could be explained as a function of its coordination to the tetrahedral titanodioxirane species. In presence of $H_2O_2$, TS-1

**Scheme 30**



behaves as a Brönsted acid catalyzing the opening of the epoxides by addition of $H_2O$ or alcohol.[346] This fact suggests that the active species involves a tetrahedral hydroperoxy type ligand (Scheme 29). On the other hand, the stability achieved by the pentacyclic structure (Scheme 30) makes possible the acid dissociation.

The dependence of the reaction rate on the nature of the solvent seems to indicate that a molecule of solvent is involved with the active species.[353] Moreover, the cyclic hydroperoxy species is similar to the intermediates proposed in oxidation reactions with organic peracids and the transition metal complexes of groups IV−VI, with $H_2O_2$ or organic hydroperoxides.

**b. Large Pore Ti-Zeolites.** Owing to the relatively small pore diameter of the 10-member ring Ti-zeolites synthesized, i.e., TS-1, TS-2 (MELS structure) and ZSM-48,[355−357] efforts have been made to synthesize large pore 12-member ring Ti zeolites. Among them the incorporation of Ti by direct synthesis has been demonstrated for BEA (Ti-Beta), MTW (Ti-ZSM-12), ISV (Ti-ITQ-7), and MWW (Ti-MCM-22).

Ti-Beta can be prepared by several synthetic procedures. The first Ti-Beta was prepared in basic medium, in the presence of Al in the synthesis gel. [358,359] The resulting material was active and selective for the oxidation of olefins, alcohols, alkanes, and organic sulfur compounds and hydroxylation of phenol with $H_2O_2$ or organic peroxides.[360−362] By means of IR and UV−Visible spectroscopy, XRD, thermal analysis, XPS, EXAFS-XANES, the state of Ti in the sample of Ti-Al-Beta was established.[363] In the calcined and dehydrated sample the coordination of Ti is four, and in this coordination state Ti is linked to four O−Si groups. When the calcined zeolite was rehydrated a Ti−O−Si bond becomes hydrolyzed, giving a tetrahedral species with a Ti−OH group and a silanol group. This Ti−OH species can be further hydrated leading to pentacoordinated Ti. When the characterization results for Ti−AlBeta and TS-1 and TS-2 were compared, it was shown that in the calcined and dehydrated samples a similar coordination of Ti occurs. While Ti−AlBeta was an active oxidation catalyst, the presence of Al(IV) generated Brönsted acid sites that have, for some reactions, a negative impact on selectivity. For instance, during the catalytic epoxidation of olefins, the resulting epoxides undergo acid-catalyzed ring opening to afford diols and/or rearrangement products. However, the Brönsted acidity could be neutralized by treatment with alkali metal acetates.[364] While in some cases the preparation of bifunctional catalysts involving a proton and a Ti site can be of interest as in the production of furanes and pyranes derived from linalool,[365] in most cases the epoxide is the desired product. Therefore, there was the need for synthesizing Ti−Beta free of $T^{III}$ elements. Following a cogel synthetic procedure, samples of Ti-Beta with very high Si/Al ratios were synthesized and an increase in turnover number and selectivity to epoxide during epoxidation of 1-hexene and activity in the hydroxylation of benzene with $H_2O_2$ was observed when increasing the Si/Al ratio.[366,367] The following step toward the synthesis of Al-free Ti-Beta samples was given by starting with very small Al free seeds of Beta zeolite and using them to grow Al-free Ti-Beta.[368] A similar procedure but using deboronated boron Beta seeds and di(cyclohexylmethyl) dimethylammonium hydroxide as structure directing agent (SDA) was used to prepare $T^{III}$ free Ti-Beta.[369] The resulting sample was active as epoxidation as well as Lewis acid catalyst for the gas-phase Meerwein−Ponndorf−Verley reactions.[370] Finally, Al free Ti-Beta has been synthesized in basic medium using 4,4′-trimethylenebis(*N*-benzyl-*N*-methylpiperidinium) dihydroxide or di-(cyclohexylmethyl)-dimethylammonium hydroxide as SDA. [371−373] The above SDA are difficult to synthesize and it would be of interest to obtain Al-free Ti-Beta using the commercially available TEA hydroxide as SDA. This has been achieved by using $F^-$ as silica mineralizing agent. [374] It has to be pointed out that while Ti-Beta synthesized in $OH^-$ media resulted in samples with many internal defects (silanol groups) and therefore with a more hydrophilic zeolite, the synthesis in $F^-$ media gave Ti-Beta samples that were highly hydrophobic that gave the best turnover and epoxide selectivity during the epoxidation of olefins (see Table 2). [375]

**Table 2. Influence of Al Content and Internal Defects on the Activity and Selectivity of Ti-Beta for the Epoxidation of 1-hexene Using Methanol as Solvent**[a]

| synthetic method | internal defects | chemical composition Si/Al | chemical composition wt % $TiO_2$ | TOF mol/(mol Ti.h) | epoxide selectivity (%) |
|---|---|---|---|---|---|
| first synthesis | yes | 123 | 4.8 | 14.9 | 14.6 |
| cogel procedure | yes | 300 | 4.7 | 20.8 | 25.9 |
| dealuminated seeds | yes | ∞ | 2.5 | 28.6 | 75.4 |
| $F^-$ media | no | ∞ | 2.5 | 32.2 | 96.4 |

[a] Taken from ref 375.

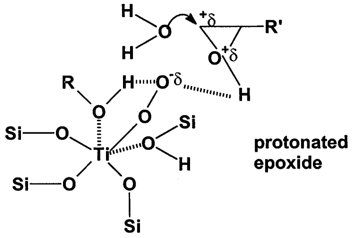
It becomes clear that in an oxidation process that requires the simultaneous presence of nonpolar (1-hexene) and polar ($H_2O_2$ aq) reactants within the zeolite pores, the hydrophobicity−hydrophilicity of the catalyst will play an important role. In the case of TS-1 the hydrophobicity of the final sample is influenced by the presence of nonframework titanium.[376] Nevertheless, even for hydrophobic Ti-Beta its activity and selectivity are still lower than those for TS-1 for molecules that can diffuse in TS-1. Nevertheless, Ti-Beta gives a higher activity for bulkier reactants. This means that besides hydrophobicity other structural factors also play an important role. In this respect, one should take into account that in solid−liquid-phase processes, diffusion can be in many cases a limiting step, and consequently, a catalyst factor to be considered, besides pore diameter, is the zeolite crystal size. The smaller the crystallite size, the faster will be the rate of diffusion for molecules that can diffuse through the pores. Ti content may influence the zeolite crystal size, decreasing this when increasing Ti content in TS-1.[377,378] It has been found that the synthesis variable that has a stronger impact on Ti-zeolite crystal size is the nature of the mineralizing agent. This has been studied for both TS-1 and Ti-Beta, and it is shown that synthesis in $F^-$ media generally produces larger crystallites than the synthesis in $OH^-$ media.[379−381]

The intrinsic acidity of the Ti Lewis sites in a particular structure and even in different T positions of a given zeolite structure can also influence the final activity of the catalyst. A theoretical study on the Lewis acidity of Ti on the different crystallographic positions in silicalite and Beta has concluded[382] that Ti will not necessarily occupy framework positions in a random distribution. Moreover, differences on the Lewis acidity of Ti are expected depending on the different crystallographic positions. It has to be pointed out that, in general, the calculated Lewis acidity of Ti in the Beta structure is higher than in TS-1. Experimentally, the acidity of Ti-zeolites has been studied by means of IR spectroscopy[383] volumetry and microcalorimetry[384,385] of adsorption of weak (CO) and stronger bases ($NH_3$, pyridine, $CD_3CN$). In the particular case of TS-1, the spectrum of adsorbed pyridine shows bands at 1605, 1490, 1445 $cm^{-1}$ associated to adsorption on Lewis acid sites,[386] but not the band at 1545 $cm^{-1}$ which corresponds to the protonated pyridine. The presence of Lewis acid sites in TS-1 and TS-2 has also been confirmed by other techniques,[387] which also include their activity for Mukaiyama and Michael additions, and Meerwein−Ponndorf−Verley reactions that are typically catalyzed by Lewis acids.[340,370,388] In the case of Ti-Beta zeolites, the IR spectra of pyridine adsorbed on two samples of Ti-Beta, one synthesized in $OH^-$ and the other synthesized in $F^-$ media have been recorded.[379]

The Al-free Ti-Beta synthesized in $OH^-$ media with many internal defects and which has a certain hydrophilic character shows bands at 1607, 1490, and 1447 $cm^{-1}$ associated to pyridine coordinated with Lewis acids, and which are the same bands observed previously for TS-1. With the more hydrophobic samples synthesized in $F^-$ media, the same bands but with a lower intensity are observed. Since none of these IR bands were observed with the pure silica Beta zeolite, we concluded that they are associated with pyridine coordinated with Ti.

The nature of the Lewis acid sites in Ti-zeolites is still a matter of discussion. Some authors believe that the observed Lewis acidity in Ti-zeolites is due to the presence of Ti(IV) in framework positions,[386,389] while others claim that the Lewis acidity is associated to $Ti^{4+}$ ions within framework defects. We can make use of these hypotheses to explain differences in the intensity of the IR bands. Thus, since Ti in defects would be more accessible to pyridine than Ti incorporated in framework positions, one may assume that Ti-Beta synthesized in $OH^-$ media should have a larger concentration of Ti in defect sites than the sample synthesized in $F^-$ media. On the other hand, taking into account that pyridine was desorbed at 150 °C and $10^{-4}$ Torr before recording the IR spectra, and also that the two samples have the same Ti content, one can conclude that the Ti-Beta synthesized in $OH^-$ media has stronger Lewis sites than those for the sample prepared in $F^-$ media. The observed differences in acid strength could explain the larger extent of epoxide ring opening that occurs in absence of $H_2O_2$, with Ti-Beta synthesized in $OH^-$ media. On the other hand, when in the presence of $H_2O_2$, it can be assumed that the epoxide ring opening occurs in Ti-zeolites through the transition state shown in Scheme 31.

**Scheme 31**



In this case, the different Lewis acidity in the two samples can also explain the higher epoxide ring opening of Ti-Beta $OH^-$, in methanol and $H_2O_2$. Indeed, the higher the acid strength of the Ti Lewis sites, the higher will be the inductive effect and the acidity of the "proton" of the hydroperoxo group coordinated to the metallic atom.

It becomes then clear that one should not discuss about Ti-Beta and any other Ti-zeolite without taking into account factors such as Ti-content, synthesis procedure, and their implications on hydrophobicity/hydrophilicity and acid strength/Ti-distribution.

Even if most of the work in Ti-zeolites has been done with TS-1, TS-2, and Ti-Beta, other large pore Ti-zeolites have been prepared by direct synthesis. Among them we can mention Ti-ZSM-12, Ti-ITQ-7 and Ti-MCM-22. Ti-ZSM-12, a unidimensional zeolite, has been described using hexamethylene-bis-(diethylmethylammonium hydroxide) as SDA.[390] Ti-ITQ-7 is a tridimensional large pore zeolite in which small amounts of Ti were introduced with low efficiency.[391,392] A much more efficient synthesis that allows the introduction of higher Ti contents and with higher intrinsic activity has been described and involves the synthesis of Ti-Ge-ITQ-7 zeolite.[393−395] Very recently, Ti-MWW (Ti-MCM-22) has been prepared by direct synthesis and after acid leaching of part of the Ti, the resulting sample shows high activity and selectivity for oxidation of small molecules.[396,397] Finally, a delaminated Ti-ferrierite named as Ti-ITQ-6 has been synthesized with external surface areas $\geq 600\ m^2\ g^{-1}$.[398] This material can carry out oxidation reactions with $H_2O_2$ and organic peroxides. Moreover, the delaminated accessible structure allows the reaction of bulky organic reactants that can hardly diffuse in the internal pores of zeolites.

Other large pore zeolites such as FAU, MAZ, LTL and delaminated ITQ-2 zeolite,[399] MOR, and MWW[396] have been prepared by postsynthesis methods.

### 8. Mechanism of Electrophilic Oxidations Catalyzed by Ti-Zeolites

To elucidate a reaction mechanism in heterogeneous catalysis, it helps very much to stablish analogies with homogeneous systems, for which reaction mechanisms at the molecular level are easier to study. If one applies this methodology to electrophilic oxidations, some trends appear clear and they are summarized as follows:[400]

(a) Complexes that catalyze the nonradical epoxidation of simple alkenes with $H_2O_2$ or alkyl hydroperoxides are almost always Lewis acids.

(b) Complexes containing a transition metal with an empty d-shell, as for instance Mo(VI), Ti(IV), Re(VII) in $CH_3ReO_3$, are effective Lewis acids.

(c) In all known peroxo complexes of the group IV–VII transition metals, the peroxo moiety is bonded side-on.

(d) Besides a three-membered ring (metallodioxirane structures), oxygen can be transferred smoothly from five-membered ring structures.

(e) Metal-catalyzed epoxidation and epoxidation by peracids experience similar solvent effects: polar solvents enhance the reaction rate except for strongly coordinating or protic solvents which slow or completely inhibit the reaction.

In the case of oxidations using Ti-zeolites, any valid mechanism should also consider the effects of solvents, and the fact that the active species possesses Brönsted acidity and ion exchange properties. The reaction mechanisms for three types of important reactions occurring with Ti-zeolites are described in the following sections.

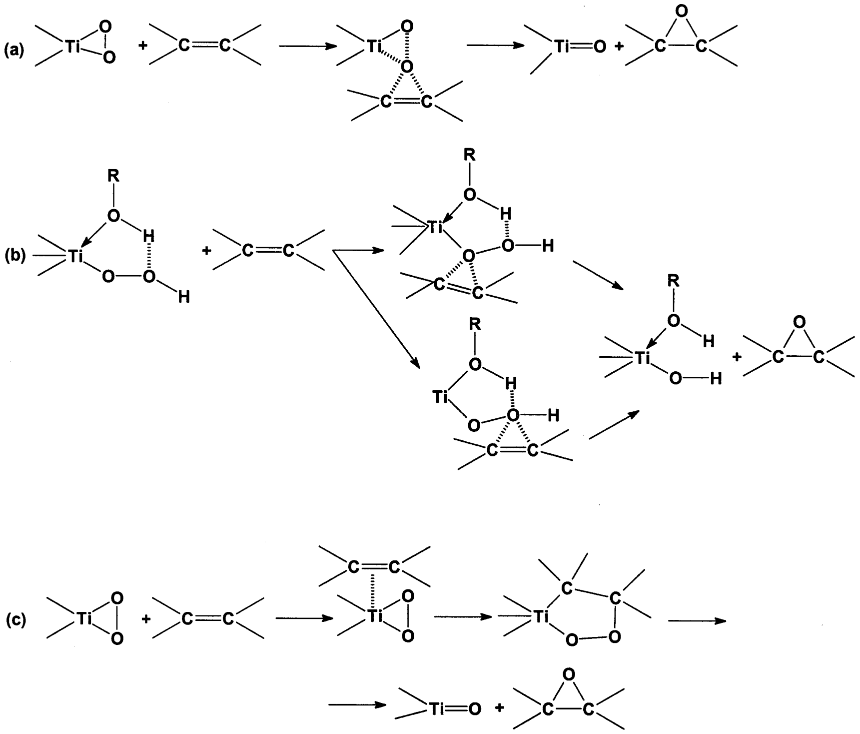
**a. Olefin Epoxidation.** Olefins are epoxidized in the presence of Ti-zeolites using diluted $H_2O_2$ as oxidant. The absence of products derived from radical epoxidations (allylic alcohols) and the stereospecificity of the reaction (cis-olefins produce cis-epoxides) indicate the nonradical nature of the epoxidations occurring on Ti-zeolites. The different reaction mechanisms proposed for the epoxidation of olefins with $H_2O_2$ with Ti-zeolites are indicated in Scheme 32.[341,353,401]

By analogy with soluble complexes of Mo(VI), W(VI), and Ti(IV) mechanisms a and b in Scheme 32 imply an electrophillic attack of titanodioxirane and hydroperoxy species to the olefin. Mechanism b in Scheme 32 can occur through two intermediates, and there is discussion about which oxygen is transferred to the olefin. Mechanism c in Scheme 32 implies the direct coordination of the double bond to the Ti center. However, it appears that in the presence of $H_2O$, alcohols, and other oxygenated molecules it is not very probable that Ti(IV) could coordinate with an olefin that is a much weaker coordinating ligand.

In contrast to homogeneously catalyzed epoxidation in which the reaction rate is mainly governed by electronic factors, steric factors having only a minor influence, in the case of epoxidation catalyzed by Ti-zeolites, steric factors such as the bulkiness of substituents attached to the C=C double bond can sometimes dominate.[353,402,403]

**b. Alcohol Oxidations.** As was said above, the interaction of Ti centers and $H_2O_2$ in the presence of a solvent of the ROH type can generate a five-member cyclic structure that can be considered the active species. Taking this into account, it may very well occur that in the presence of other alcohols similar structures are formed. These type of structures have an electrophilic character owing to the presence of a partial positive charge on the oxygen situated far away from the Ti and which is activated by the formation of the hydrogen bond. However, the oxidation of alcohols requires activation of the C–H

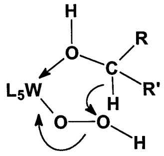
**Scheme 32**



bond, and, consequently, the reaction intermediate should have a structure in where the C−H bond is weakened.

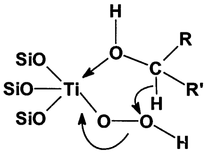
In the case of alcohol oxidations by W complexes, Jacobson et al.[404] have proposed the species shown in Scheme 33 as potential intermediate.

**Scheme 33**



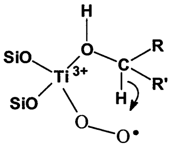
In this intermediate, the heterolytic rupture of the C−H occurs concurrently with the nucleophilic attack of the hydride ion on the most distant oxygen. Taking the above structure as a model, Esposito et al.[405] have proposed a similar intermediate for the oxidation of alcohols with $H_2O_2$ with TS-1 (Scheme 34).

**Scheme 34**



A radical mechanism having as key intermediate the structure shown in Scheme 35 has also been proposed for the oxidation of alcohols.[406]

**Scheme 35**

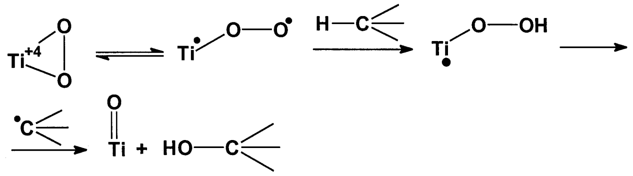


In both types of mechanisms, the alcohol coordinates to the Ti before hydride or hydrogen abstraction takes place. This can explain the observed differences in the rate of oxidation between 2-pentanol and 3-pentanol (the latter reacting 10 times more slowly) in the TS-1,[406] and consequently none of the two mechanisms can be rejected. Nevertheless, the high selectivities to aldehydes favor the two-electron process. Otherwise, aldehydes would undergo a fast oxidation to carboxylic acid derivatives. It is interesting to notice that alcohol oxidation by neutral or anionic tungsten or molybdenum peroxo complexes is also widely accepted as a two-electron process.[407] The molybdenum picolinate *N*-oxide complex $MoO(O_2)_2(pico)^-$ is especially selective to aldehydes. It is not clear to what extent heterolytic alcohol oxidation by peroxo complexes should still be considered an "electrophilic" reaction, since it is commonly said that less electrophillic reagents are needed to effect alcohol oxidation compared to alkene epoxidation.

**c. Alkanes Oxidation.** TS-1 is an active zeolite for the gas-phase oxidative dehydrogenation of propane to propene.[408] For this medium pore titanosilicate, the reaction takes place on the outer surface of the solid particles on Lewis acid sites. Sulfation of the catalyst increases the acidity of external Lewis acid sites and results in an increase in the catalytic activity. Addition of water also causes an increase in the selectivity of the process, probably due to the competitive adsorption on the active sites. The maximum conversion was 17% with a selectivity to propene of 74%.[408]

It was found independently by two groups[409,410] that TS-1 was able to oxidize alkanes to secondary alcohols and ketones. To explain such results, Huybrechts et al. proposed the radical mechanism, which is very similar to that proposed for oxidation with vanadium complexes (Scheme 36).[411]

**Scheme 36**



A radical mechanism for this reaction was supported by the fact that the oxidation of *cis*-1,3-dimethylcyclopentane on TS-1 proceeds without any stereoselectivity.[412] The formed radicals, however, have a very short lifetime or their movements are highly restricted in the pores of TS-1 since their rearrangement is not observed. A radical mechanism was also consistent with the low reactivity of the terminal carbons. On the other hand, a radical mechanism for oxidation of alkanes implies the formation of $Ti^{3+}{-}OO^{\bullet}$ radicals, that require the reduction of $Ti^{4+}$, something that is improbable owing to the low redox potential of $[Ti^{4+}/Ti^{3+}]$ (0.06 eV). Nevertheless, if the energy of formation of the O−H of the TiOOH is high and comparable to the C−H energy, the radical mechanism could take place.[413] Also at the relatively high temperature used by Huybrechts et al.,[409,414] the participation of radicals and molecular oxygen in the process can be important.

It is remarkable that Clerici,[410,415] by working under milder conditions, obtained somewhat different results than Huybrechts et al. (see Table 3).

Clerici observed that the addition of radical chain inhibitor or chloroalkanes did not influence reaction rates or product distributions.[410] Following this, a free-radical chain mechanism can be considered less likely, at least, under the milder conditions used by Clerici.[410] Evidence for the electrophillic nature of the process was obtained from the oxidation of 1-chloro-

**Table 3. *n*-Hexane Oxidation with $H_2O_2$ on TS-1**

| ref | Huybrechts et al.[414] | Clerici[410] |
|---|---|---|
| solvent | acetone (two phases) | methanol (one phase) |
| temperature, °C | 100 | 55 |
| $H_2O_2$ conversion (%) | > 90 | 98 |
| sel based on converted $H_2O_2$ (%) | 70 | 91 |
| (2-ol + 2-one)/ 3-ol + 3-one) | 1.1 | 2.3 |

hexane and methyl heptanoate, in which oxygenation occurred preferentially on the remote secondary C−H bond.[409]

It is not yet completely clear what the mechanism of the oxygen insertion reaction is, and whether it consists of two consecutive one electron steps or a single two electron step. It should be taken into account that reactions involving a hydrogen abstraction step followed by a fast recombination of radicals in a so-called "solvent cage" are known.[416] Such solvent cage reactions are also not affected by radical chain inhibitors or chloroalkanes. This solvent cage mechanism would be supported in the case of TS-1 in which a large isotope effect ($K_H/K_D = 4.1$) was observed.[410]

### *9. Other Transition Metal Containing Zeolites and Other Microporous Molecular Sieves*

The very interesting catalytic results obtained with Ti-zeolites acted as a booster for the synthesis of zeolites containing other transition metals within framework positions. Similarities between vanadium and titanium in their catalytic peroxo chemistry have influenced the synthesis of vanadium silicalites. The known coordination chemistry of vanadium does not rule out their ability to occupy tetrahedral lattice positions in a silicate. However, the usual coordination geometry of vanadium (IV) is square pyramidal or distorted octahedral. Compounds containing tetrahedral vanadium (IV) are rare. Tetrahedral coordination is also rare for vanadium (III), one example being the $VCl_4^-$ ion that occurs in some salts. Nevertheless, it has been claimed the synthesis of vanadium-containing MFI and MEL silicalites starting from V(III) or V(IV) salts.[417] It has been reported[346] that vanadium-containing zeolites and silicalites prepared using $VCl_3$ underwent a structural collapse leading to the formation of crystobalite after calcination at 550 °C in air. This did not occur if the calcination was done in $H_2$ atmosphere. The structure collapse can be due to the oxidation of V(III) or V(IV) species very well dispersed in the zeolite matrix. Stable materials were obtained when the synthesis was done in the absence of sodium, using vanadyl(IV) sulfate and avoiding oxidation of V(IV) during gel preparation and crystallization.[418,419]

Other zeolite structures such as ZSM-48 and V-NCL-1 have been synthesized, and the resulting materials were stable after several calcinations in air.[420,421]

The existence of V−O−Si bonds in vanadium-containing zeolites has been postulated from the presence of the IR and Raman band at 960 $cm^{-1}$, as well as by a direct correlation between vanadium content and unit cell expansion.[422] Adsorption of $NH_3$, pyridine, and acetonitrile shows the presence of Lewis and Brönsted acids in V-MFI and V-MEL that were not present in the pure silica zeolites.[423,424]

ESR spectroscopy gives information about the state of the vanadium in the zeolite. Thus, ESR spectra of V(IV)-containing samples show anisotropic hyperfine splitting caused by the $^{51}V$ nucleus with or without the presence of an underlying broad singlet. The singlet is thought to arise from vanadium-rich phases or oligomeric species, while the hyperfine pattern originates from isolated ions. The values of the ESR parameters fall within the range reported for square pyramidal vanadyl complexes in an oxygen environment. However, vanadyl species cannot be located at a regular tetrahedral framework site and they may exist as a framework satellite.

In situ reflectance spectroscopy has been used for studying the coordination environment of vanadium during the synthesis of VAPO-5.[425] $^{51}V$ NMR spectroscopy is also useful for elucidating the local symmetry of V(V) species. This technique shows that in most calcined vanadium silicalites, V(V) is present in tetrahedral coordination.[426,427]

It appears then that it is possible to prepare vanadium-containing zeolites in which isolated vanadium species may be connected to the framework at defect sites forming framework satellites. These vanadium atoms are accessible to molecules that can enter into the pores, and can apparently change its coordination and oxidation state reversibly.

Chromium would be an interesting Lewis acid that could carry out oxidation reactions if it were tetrahedrally incorporated in zeolites. It has been claimed isomorphous framework silicon substitutions by chromium in MFI structure.[428−430] However, no effect of chromium on unit cell parameters were found, indicating that chromium species are not really in the framework or the efficiency of chromium incorporation in the framework is very low..[431,432] Zn, however, has been incorporated in Beta zeolite, and it occupies preferentially three-member rings. This material presents Brönsted acidity owing to charge compensation.

In the case of $AlPO_4$ molecular sieves isomorphous substitutions with cobalt, vanadium, iron, chromium, manganese, and zinc have been well documented. Aluminophosphates molecular sieves containing Si, V, Co, and Mn have been synthesized using *n*-dipropylamine as a template.[433] The presence of these elements in framework positions considerably influences the physical and catalytic properties of the materials. By using the methylation of toluene and isomerization of *m*-xylene as test reactions, it was found that the product distribution of Si or metal substituted AlPO-11 is similar to that of zeolites.[433] AlPO-11 not containing any heteroatom fails to exhibit any activity for these reactions, although it shows activity for less-demanding isobutanol dehydration. This study concludes that metal substitution on AlPO-11 introduces additional stronger acid sites by replacing framework $Al^{3+}$ by divalent metal atoms. These sites are stronger than in the case of the Si-containing AlPO, but much weaker than those of zeolites.[433] On the other hand, metal substituted AlPOs also exhibit activity in the hydrogenation of nitrobenzene and oxidation of benzylic alcohols, thus, demonstrating the redox properties imparted to the solid by the presence of framework metal sites.[433]

Isomorphic substitution of Al by Mn(II), Co(II), and Zn(II) in $AlPO_4$-31 has been confirmed by $^{31}P$ NMR spectroscopy.[434] In the case of MnAPO-31 UV−Vis and XANES spectra revealed the partial oxidation of some Mn atoms into Mn(III) in calcined samples, introducing redox centers in the solid. The presence of Brönsted and Lewis acid sites was studied by ammonia adsorption/desorption titration and the relative strength follows the order MnAPO-31 > CoAP-31 > ZnAPO-31. In contrast, Ti(IV) is not incorporated into the framework and the presence of $TiO_2$ anatase was observed.[434]

Low levels of Co(II) can be incorporated into the framework of AlPOs substituting aluminum on tetrahedral positions as shown by UV−Visible, near-IR, ESR, and $^{31}P$ NMR techniques and EXAFS.[305,435−441,442] During calcination in the presence of $O_2$, tetrahedral cobalt (III) and strongly distorted tetrahedral cobalt (II) species are formed in CoAPOs. The oxidized species can be reduced back to tetrahedral cobalt (II) by calcination in $H_2$.

A UV−Vis and FT-IR spectroscopic study combined with the use of probe adsorbates has suggested that there are two types of cobalt atoms in CoAPO-18.[443,444] Besides tetrahedrally coordinated framework Co atoms, there are coordinatively unsaturated Co(II) Lewis acid centers. Approximately one-half of the tetrahedral framework Co atoms form bridged hydroxy Co(OH)P groups that introduce Brönsted acidity to the solid and that are able to undergo oxidation to framework Co(III).[445]

A well-crystalyzed sample of CoAPO-37 having faujasite structure has been prepared.[446] The incorporation of Co in the framework introduces Brönsted and Lewis acid sites as shown by pyridine titration recorded by IR spectroscopy. Catalytic tests reveal that CoAPO-37 has activity for 1-butene and *m*-xylene isomerization, indicating that the acid sites of CoAPO-37 are stronger than those of SAPO-37 and similar to those of Y zeolites.[446]

VAPO-5 has been synthesized with well-dispersed monomeric vanadyl(IV) species which were oxidized to vanadium(V) after calcination in air at 773 K. The presence of well-dispersed, immobile vanadium species was taken as evidence of the location of the metal in framework positions.[447,448] Those authors assumed, on the basis of elemental analysis, that vanadium(IV) substituted phosphorus (V). However, Rigutto et al.[449] synthesized VAPO-5 in $F^-$ media using vanadyl(IV) sulfate as the vanadium source. By means of $^{51}V$ NMR spectroscopy, it has been shown that at low vanadium contents the dominant species in calcined materials is a square pyramidal or distorted octahedral vanadyl(V) species, consistent with a phosphate environment.

Chromium has also been introduced in $AlPO_4$'s in octahedral positions and/or as framework connected ions. Diffuse reflectance UV−Visible spectroscopy seems to indicate that octahedral chromium(III) are present in as-synthesized CrAPO-5 which is oxidized to tetrahedral chromium(VI) upon calcination.[450,451] The incorporation of $Cr^{3+}$ in $AlPO_4$-16 framework is also uncertain, and two species are observed: clusters similar to the bulk $Cr_2O_3$ oxide and isolated $Cr^{3+}$ ions in strongly distorted octahedral coordination. [435]

Cr-substituted aluminophosphates (CrAPO-5 and CrAPO-11) in which chromium atoms occupy internal framework positions have been hydrothermally synthesized and found selective and reusable solids for the catalytic oxidation of benzylic and cyclic alcohols using oxygen or *tert*-butyl hydroperoxide as oxidants.[452] Evidence was provided in support that the oxidation essentially takes place within the micropores through a mechanism involving a oxochromium alkoxide. This active species undergoes a heterolytically $\beta$-hydrogen elimination followed by reoxidation of Cr(IV) to Cr(VI).[452] Using *tert*-butyl hydroperoxide, high selectivities of the oxidizing reagent (>88%) and substrate (>89%) toward the ketone were observed. The CrAPO-5 catalyzed oxidation of alcohols with $O_2$ gives also the corresponding ketones with 72−97% selectivity at 26−78% conversion when only 10 mol % of *tert*-butyl hydroperoxide was added.[452]

A study aimed at characterizing and determining the activity of framework Cr atoms incorporated into silicoaluminophosphate molecular sieves has been undertaken.[453] Compared to a catalyst in which Cr has been supported on SAPO-11, XPS and diffuse reflectance UV−Vis spectroscopy indicates that approximately 70% of Cr atoms are in the +VI oxidation state. After hydrogen reduction at 550 °C, the distribution of Cr atoms was approximately 40% as Cr(VI) and 60% as Cr(III). This reduction decreases the number of strong Brönsted and strong and medium Lewis acid sites of CrAPSO-11 by a factor of 2. These results seem to indicate that partially unsaturated Cr(VI) in the neighborhood of P−OH groups may act as strong Lewis sites and may generate strong Brönsted acid sites by Lewis enhancement of Brönsted acidity. In comparison, the main Cr species present in a sample of Cr-supported SAPO-11 was Cr(III) and reduction was easier. All the available data support as previously reported by Chen and Sheldon[454] that Cr atoms are incorporated into the framework of the molecular sieve.[453]

In general, it can be said that the thermal stability of the metal ALPOs (MeAPOs) is lower than for zeolites and upon calcination a significant portion of the metal can migrate from framework to nonframework positions. The formation of nonframework metal can be complete upon succesive cycles of calcination. The presence of nonframework metals favors the leaching of the metal when the catalytic oxidation is carried out in the liquid phase.

A titanoaluminophosphate in which the titanium atoms occupy octahedral framework positions has been obtained by adapting the hydrothermal synthesis of VPI-5 aluminophosphate in the presence of di-*n*-butylamine.[455]

Crystalline vanadium silicates (Si/V 79−161) with MEL structure may have a single vanadium species according to the $^{51}V$ NMR wherein a single peak at −573 ppm having a width of 50 ppm is observed.[456] These spectroscopic parameters correspond to tetrahedrally coordinated $V^{4+}$, thus, ruling out the presence of $V_2O_5$ clusters in these solids. A linear increase in the intensity of the ESR peaks with the vanadium content was also observed. The solids possess both Brönsted and Lewis acid sites as evidenced by the pyridine adsorption method. These vanadium silicates oxidizes toluene to a mixture of cresols, benzylic alcohol, and benzaldehyde.[456] The internal location of the V ions inside the channel system of the MEL zeotype was demonstrated from the differences in the oxidation rates for xylene isomers.[456]

Tin has been claimed to be introduced in framework positions of MFI, ZSM-12, ZSM-48, and Beta zeolite.[457−463] In zeolites, Sn tends to be located in satellite positions, i.e., in defects. With a sample of Sn-Beta synthesized with enriched $^{119}$Sn, it has been found by $^{119}$Sn NMR that the metal adopts a 6-fold coordination when the solid is hydrated, and changes to a four coordination upon dehydration.[463] The activation of the Sn-zeolites is critical. Overheating during calcination brings about structure stabilization and at the same time a partial ejection of framework Sn occurs. Calcination in “shallow bed” at temperatures not higher than 773 K allows the Sn to stay attached to the framework in tetrahedral coordination.[459,464,465]

### *10. Catalytic Activity of Microporous Molecular Sieves with Framework Transition Metals for Oxidation Reactions Using Peroxides*

**a. Epoxidation of Olefins.** Ti-zeolites and more specifically TS-1 have been the most successful transition metal containing zeolites from a catalytic point of view. The use of $H_2O_2$ is environmentally adequate, but the process is complicated by its inmiscibility with organic solvents. The presence of accompanying water that can promote hydrolysis can also be a limitation. TS-1 and Ti-Beta catalysts have shown to be active and selective for olefin epoxidation with $H_2O_2$. Ti-Beta, with a lower intrinsic activity than TS-1, can epoxidize bulkier olefins than TS-1 owing to the large pore diameter of the former. The use of TS-1 for production of propylene oxide would allow the use of $H_2O_2$ instead of the organic hydroperoxide used in ARCO and SHELL processes. It has to be remarked, however, that while $H_2O_2$ gives a higher flexibility, the use of the organic peroxides in ARCO and SHELL processes can also be economically interesting if there is a market for the products formed. Recently, Sumitomo has presented a new technology in which the organic peroxide (cumene hydroperoxide) is produced in the plant by reoxidation of the alcohol formed when transferring the oxygen from cumene hydroperoxide to the propylene.[466−472]

In the case of propylene oxidation with $H_2O_2$ at 313 K using methanol as solvent, 95% of the $H_2O_2$ is reacted with 90% selectivity to propylene oxide. The byproducts formed are mainly propylene glycol and its monomethyl ethers. These reactions are catalyzed by residual Brönsted acidity or even by the Lewis acidity of the Ti. Therefore, improvements in selectivity are obtained by partially neutralizing catalyst acidity. Obviously, the catalyst deactivates with time of use.[333] This deactivation is mainly due to the strong adsorption of glycol on Ti that competes with reactants for adsorption sites. The catalyst can be regenerated by eliminating the adsorbed products by calcination or by washing with alcohols, or by refluxing the catalyst with dilute $H_2O_2$.[473] EniChem has designed a new process for the one-step epoxidation of propylene to the epoxide using TS-1 catalyst. The technology, based on a slurry process, is highly selective and generates a limited amount of byproducts.[474] Degussa has also announced a process for the epoxidation of propylene to the epoxide.

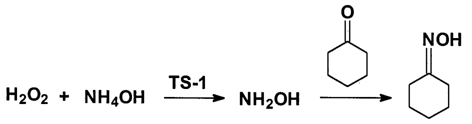
The TS-1 oxidation of larger alkenes is diffusion-limited and then there is one opportunity for Ti-Beta which has larger pores to be more active than TS-1. In this sense, Tatsumi et al.[475] showed that during oxidation of *n*-paraffins with $H_2O_2$ in the presence of TS-1 catalyst, the rate of oxidation decreased when increasing chain length due to diffusional limitations. In the case of *n*-olefins, Corma et al.[361] found that when increasing the chain length of *n*-olefins at least up to $C_{12}$, the turnover number (mol/mol Ti h) for epoxidation increased with TS-1, but selectivity to epoxide decreased. In the case of Ti-Beta, turnover number also increased, but this increase was larger than with TS-1. In other words, it seems that Ti-Beta, especially when properly synthesized and subject to a postsynthesis treatment,[476] gives higher activities and selectivities than TS-1 for olefins with 8 or more carbons. However, the preferred solvent for Ti-Beta is acetonitrile instead of methanol which in turn is more suitable for TS-1. An example of the benefit of the larger pores of Ti-Beta for the epoxidation of long chain *n*-olefins and bulky olefins corresponds to the epoxidation of methyl oleate and linalool for the production of chemicals and fine chemicals.[362,477]

Ti-Beta zeolites within a wide range of Ti and Al contents were used for the selective oxidation with $H_2O_2$ of *n*-hexane to ketones, cyclohexane to adipic acid, octanol to octanoic acid, cyclopentanone to glutaric acid, and the side chain oxidation of toluene.[478] *n*-Hexane conversions of 2−10% were achieved, the products formed being the 2- and 3-alcohols and ketones. A 25% yield of adipic acid with 55% selectivity was obtained for the oxidation of cyclohexane with Ti-Beta and $H_2O_2$. The oxidation of toluene gave 19% yield of side chain oxidation in a total selectivity of 76% with nearly equal amounts of benzyl alcohol, aldehyde, and acid. Ti-Beta was much superior than TS-1 for oxidation to acids. TS-1, on the other hand, was a good catalyst for conversion of allyl chloride to epichlorohydrin with diluted $H_2O_2$. The conversion of peroxide was 80% with an epoxide selectivity of 90%.[479] $\alpha$-Methylstyrene is converted to acetophenone using TS-1 and TS-2.[480]

Novel layered zeolites with a very large external surface area and a reduced microporosity have been obtained by delamination of layered zeolite precursors before calcination.[481] For instance, ITQ-6 has been obtained by delamination of the layered precursor of ferrierite, and it has a very large surface area that is accessible to large reactants. It has been possible to introduce directly by synthesis Ti atoms in framework positions. It was demonstrated that Ti occupies framework positions. The resulting Ti/ITQ-6 is active and selective for the 1-hexene epoxidation with hydrogen peroxide. Ti/ITQ-6 remains active after repeated reaction/calcination cycling.[394,398]

**b. Ammoximation of Ketones.** Ammoximation of cyclohexanone to cyclohexanone oxime is carried out by reacting cyclohexanone with hydroxylamine sulfate. This process generates one mole of $(NH_4)_2SO_4$ per mole of the oxime formed. The cyclohexanone oxime is used to produce caprolactam. EniChem has found that TS-1 is able to catalyze the reaction of hydrogen peroxide and ammonium hydroxide to form “in situ” hydroxylamine that subsequently reacts with cyclohexanone to form the corresponding oxime (Scheme 37).[482]

**Scheme 37**



Nitrogen and nitrous oxide are also formed in very low amounts. Other byproducts formed from homogeneous reactions are nitrocyclohexane, (cyclohexenyl)cyclohexanone, and cyclohexanone azine.[483] Some catalyst deactivation is observed due to the dissolution of the zeolite in the alkaline reaction media. EniChem and Sumitomo have presented a new process for the production of caprolactam that involves the use of TS-1 for producing the oxime from cyclohexanone. The reaction takes place in a continuous stirred tank reactor in *tert*-butyl alcohol as solvent. Kim et al.[484] reported that the activity of TS-1 for the $H_2O_2$ ammoxidation of cyclohexanone depended on crystallite size, titanium concentration, and the mode of addition of the peroxide. TS-1, Ti-ZSM-48, and Ti-Al-Beta were tested in the ammoximation of cyclohexanone and hydroxy aromatic ketones.[485] Ti-Beta shows catalytic properties similar to TS-1, only using a large excess of $NH_4OH$ and methanol as a solvent, because of its hydrophilic character. We have found that when hydrophobic Ti-Beta zeolites are produced and $C_3-C_4$ alcohols are used as solvent, the catalytic behavior of Ti-Beta approaches to that of TS-1.[379]

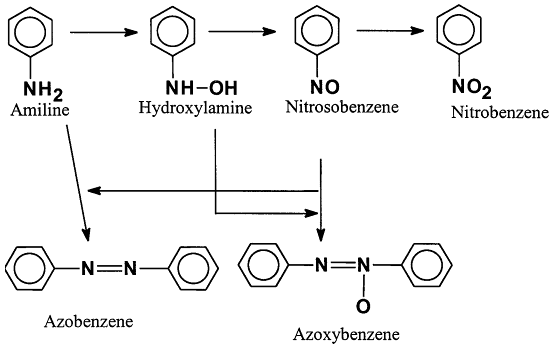
Ti-ZSM-48 owing to its monodimensional channel system gives poor catalytic results. However, Ti-mordenite prepared by a secondary synthesis method from dealuminated mordenite (Si/Al = 300) gives good ammoximation results.[486]

**c. Oxidation of Heterocompounds.** TS-1 is a good catalyst to carry out the oxidation of 2,2,6,6-tetramethyl piperidine with $H_2O_2$ to the corresponding nitroxyl compounds with 96% yields.[487] Some worse results were reported by Horchler et al.[488] during the oxidation of heterocyclic compounds such as pyrazole by TS-1 and $H_2O_2$, with yields of 34% and selectivities of 46.5%.

Aniline can be oxidized with $H_2O_2$ giving a rather complex reaction mixture[114] when using Ti-Beta and Ti-mesoporous materials (Scheme 38).[489,490]

The reaction scheme shows the formation of phenylhydroxylamine, nitrosobenzene, and nitrobenzene in a series of consecutive reactions. The condensation of unreacted aniline with nitrosobenzene results in the formation of azobenzene, while reaction of hydroxylamine with nitrosobenzene produces azoxybenzene.

**Scheme 38**

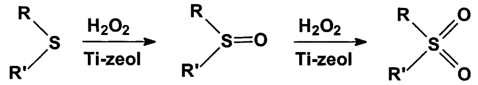


Na- and/or K-doped TS-1 catalyst has been used for the selective oxidation of diethylamine to diethylhydroxylamine with diluted hydrogen peroxide.[491−493] The selectivity to diethylhydroxylamine is highest for the K-doped TS-1, with a K/Ti atomic ratio of 1.[492] With the optimum catalyst, a selectivity to diethylhydroxylamine of 92% was measured with a $H_2O_2/(CH_3CH_2)_2NH$ ratio of 0.9. Since Ti catalyzes the oxidation of both diethylamine and diethylhydroxylamine, the results of the catalytic activity have been interpreted as reflecting the neutralization of the Lewis acid sites, thus disfavoring the adsorption of the weakest base.[492]

Tertiary amines are oxidized to the corresponding nitrogen oxides. Tosyl hydrazone undergo C=N oxidative bond cleavage with $H_2O_2$ to give high yields of the corresponding carbonyl compounds. It has been postulated that for this reaction, oxaziridines would be formed as intermediate compounds that would be oxidized to carbonyl compounds.[494]

Hydroperoxides and peracids are known to oxidize organic sulfides to sulfoxides and sulfones. However, a more friendly process involves TS-1 and TS-2 molecular sieves which efficiently catalyze the oxidation of thioethers to the corresponding sulfoxides and sulfones using diluted $H_2O_2$ as oxidant (Scheme 39).[339]

**Scheme 39**

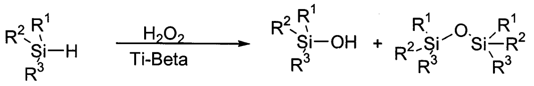


When bulkier sulfides are to be reacted, Ti-Beta and Ti-MCM-41 give a better performance than TS-1 using either $H_2O_2$ or organic peroxides.[495]

This type of reaction has been applied to the elimination of sulfur-containing compounds in the kerosene fraction.[496,497] In this case, Ti-Beta is used in the presence of $H_2O_2$ and acetonitrile as a solvent to form sulfones from sulfides and thiophenes. The more polar sulfones are washed out with water from the kerosene fraction.

Small and medium sizes silanes can be oxidized at room temperature to the corresponding silanols by $H_2O_2$ using Ti-Beta as catalyst with high conversions and excellent selectivity (Scheme 40).[402] The major advantage compared to homogeneous catalysis is the

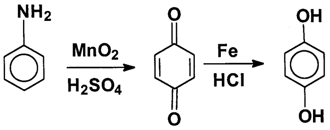
**Scheme 40**



absence of disiloxane formation due to steric restrictions. In contrast, TS-1 was found inactive for this reaction due to the lack of diffusion of reagents through the medium size pores.

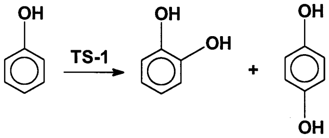
**d. Hydroxylation of Phenol.** Dihydroxybenzenes are largely used today as intermediate chemicals. They are produced by decomposition of diisopropyl benzene hydroperoxides, or by hydroxylation of phenol in strong acid media ($ClO_4H$). Hydroquinone (*p*-dihydroxybenzene) was also produced by the oxidation of aniline using manganese dioxide and sulfuric acid (Scheme 41). This was then followed by reduction using typically Fe/HCl.

**Scheme 41**



The last process gives a very poor atom economy while producing a large amount of waste.[430,498] A more convenient procedure for production of catechol (*o*-dihydroxybenzene) and hydroquinone *p*-dihydroxybenzene has been developed that makes use of TS-1 as a catalyst and $H_2O_2$ as hydroxylating agent. High conversions and selectivities are obtained (Scheme 42).[499]

**Scheme 42**



Owing to a combination of pore dimensions and solvent used, the catechol/hydroquinone ratio can be varied between 0.5 and 1.3. In aqueous acetone, the ratio is ~1.3, while hydroquinone formation prevails in methanol. At elevated phenol concentrations, even in methanol, that ratio is close to one. For observing shape selectivity based on product diffusion, there is a catalyst parameter that plays an important role, namely, zeolite crystallite size. Smaller crystal size increases diffusivity, increasing therefore the reaction rate.[500] Small crystallites have a higher external to internal surface ratio and then nonselective reactions occurring on the external surface should become more important. Following this, it was claimed that catechol was mainly produced at the external surface of TS-1 crystallite,[501] modifying the expected catechol-to-hydroquinone ratio, and producing more tars. Moreover, it was found that acetone was able to dissolve the tars formed on the external surface, while methanol was not. These results allow the explanation of the influence of the solvent on the catechol/hydroquinone (C/H) ratio by assuming that in methanol, catechol is rapidly formed on the external surface while hydroquinone formed inside the pores is formed more slowly giving high ratios C/H in the first moments. Following this, when the surface sites are poisoned by the tars formed, the catechol formed at the external surface strongly decreases producing a decrease of the C/H ratio in the products. In acetone, however, catechol was always the main component through the course of the reaction owing to the solubility of surface tars by acetone.

Another catalyst variable, especially important for phenol hydroxylation was the presence or not of amorphous material in the TS-1, and especially $TiO_2$. The presence of $TiO_2$ anatase and/or amorphous titanosilicates significantly decreases the yields of dihydroxybenzenes. Concentration of catalyst and reaction temperature have an important effect on yields, besides the obvious kinetic effect. When the concentration of TS-1 increases from 1 to 4 wt %, yield increases from 65 to 82% and tar production decreases.[502] Optimum temperature is in the range 80−100 °C for which dihydroxybenzene selectivity is still high and tar selectivity is low.[502,503]

The presence or not of a solvent and its nature is also an important variable. Acetone was seen to dissolve the tars, while acetonitrile has a negative influence.[504] Water was found to be the best solvent.[505]

Ti-Al-Beta and Ti-Beta zeolite prepared by direct synthesis gave equimolecular amounts of the two isomers,[366] and give better results than Ti-Beta or Ti-mordenite prepared by postsynthesis methods.[505] Ti-Al-mordenites prepared by hydrothermal and secondary synthesis gave also low yields for benzene hydroxylation.[506−508]

It would be very interesting to produce the direct hydroxylation of benzene with $H_2O_2$. When this reaction is carried out in the presence of TS-1 as catalyst, phenol is formed as the primary product, but conversion should be kept low to avoid formation of the secondary catechol and hydroquinone products. While acetone and methanol can be used as solvents, it has been found that the hydroxylation of benzene without any organic solvent, i.e., in a triphase system, is ~20 times faster than when using acetone or acetonitrile as solvents.[509] It is evident that for this reaction the hydrophobic/hydrophilic properties of the catalyst should be of paramount importance. Thus, a more hydrophobic catalyst should favor the adsorption of organophilic reagents (benzene) toward other more polar ones ($H_2O_2$, acetone).

In the case of the hydroxylation of substituted benzenes, electron-withdrawing groups, such as chlorobenzene, nitrobenzene, benzonitrile, benzaldehyde, and benzoic acid, reduce the rate of hydroxylation of the aromatic ring, indicating the electrophilicity of the oxidant species,[502] and very large amounts of catalyst are needed to observe some conversion.[510] While electron-donating groups should increase the rate of hydroxylation, the size of the substituents can affect the diffusion of the reactant, and a decrease in conversion may occur in more activated molecules.[410] It is with these bulkier molecules that large pore Ti-zeolites could be of more interest. Attention should be paid in Ti-mesoporous materials since a leaching of Ti in the presence of $H_2O_2$ occurs.

**e. Oxidation of Alcohols.** TS-1 and Ti-Beta catalyze the selective oxidation of alcohols with diluted $H_2O_2$ under mild conditions.[406,511−514] Ti-Beta can also oxidize alcohols using organic peroxides as oxidants.[513,514] Oxidation of secondary alcohols give high yields of the corresponding ketone, while primary alcohols produce the aldehyde. Tertiary alcohols are not oxidized but converted to alkylhydroperoxides.[406] When a double bond and hydroxy group are both present in the same molecule, TS-1 is chemoselective for the epoxidation of the double bond.[515−519]

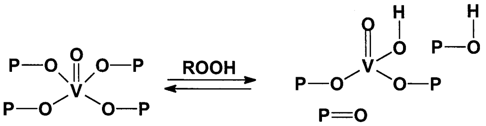
## 11. Oxidation Activity of Microporous Molecular Sieves with Metals Other than Ti

Besides Ti-zeolites, other transition metal-substituted zeolites are also active and selective for carrying out oxidations in liquid phase using either $H_2O_2$ or organic peroxides as oxidants. For instance, V-MEL silicalite is active for alkane oxidation and phenol hydroxylation. However, selectivities and $H_2O_2$ yields are lower than for TS-1.[424] V-MFI also catalyzes phenol hydroxylation and toluene oxidation with $H_2O_2$ giving a similar product distribution than V-MEL, but with lower peroxide efficiencies. V-silicalites have a higher activity than Ti-silicalites for the oxyfunctionalization of primary carbon atoms in alkanes and toluene. This indicates a more pronounced homolytic tendency of the active complex.

Vanadium mesoporous silicalites, either amorphous or ordered, have also been synthesized, showing activity for different reactions. However, they are very unstable when using $H_2O_2$ as oxidant.[520] In general, it can be said that under liquid-phase oxidation some of the vanadium is leached from the lattice, and the homogeneous reaction occurring can mask the results from the solid catalyst.[319]

VAPO-5 was found to catalyze selectively the epoxidation of allylic alcohols and benzylic oxidations with TBHP,[449] with higher eficiency than VAPO-11. On the basis of $^{51}V$ NMR studies on the interaction of vanadium species in VAPO-5 with TBHP a model was proposed for the catalytic sites of VAPO-5 (Scheme 43).

**Scheme 43**

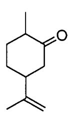
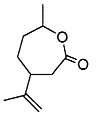
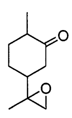
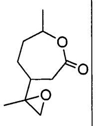


In the case of Cr substituted molecular sieves, $H_2O_2$ or alkyl hydroperoxides led to breakdown of the Si−O−Cr or Al−O−Cr bonds in substituted zeolites or AlPOs and to the leaching of some chromium in solution. Thus, most of the catalytic results that assumed that reaction was occurring in the micropores have to be reinterpreted by taking into account that an important part of the catalysis occurs with the leached chromium in liquid phase.[521]

CoAPOs have also used for liquid-phase oxidations of alkanes and alkylaromatics. Under these conditions, Co may leach if working in basic media, in the presence of organic acids or in the presence of strong polar solvents.[522,523]

Sn-silicalite is active for the hydroxylation of phenol in dilute $H_2O_2$ as oxidant. A direct correlation between the activity and Sn content up to about 2.4 Sn per unit cell was observed with a ratio of catechol to hydroquinone of 1.6. Among the different solvents used water was found the most efficient. The isolated Sn(IV) centers tend to coordinate strongly with solvent molecules such as acetone and acetonitrile reducing the solvolysis of Si−O−Sn bonds. Sn-ZSM-12 owing to its larger pores catalyzes the hydroxylation of toluene, *m*-cresol, and *m*-xylene, as well as the oxidation of methyl substituents. The product distribution and the ability of Sn-ZSM-12 to oxidize naphthalene and 2-methylnaphthalene suggest that the $Sn^{4+}$ ions are located within the channels of the molecular sieves.[458,524] Sn-AlBeta and dealuminated Sn-AlBeta were active for the oxidation of *m*-cresol and 1,3,5-trimethylbenzene with moderate selectivities and $H_2O_2$ selectivities.[461]

**Table 4. Baeyer-Villiger Oxidation of Dihydrocarvone Using Different Oxidation Systems[b]**

| Oxidant | reactant conv./% | products selectivity/% | | |
|---|---|---|---|---|
| |  |  |  |  |
| Sn-Beta/$H_2O_2$ | 68 | 100 | 0 | 0 |
| m-chloro-perbenzoic acid | 85 | 11 | 71 | 18 |
| Ti-Beta/$H_2O_2$ | 46 | 0 | 79[a] | 0 |

[a] Up to 100% were opening products of the epoxide. [b] Taken from ref 463.

Al-free Sn-Beta obtained by direct synthesis is able to catalyze the Baeyer−Villiger oxidation of cyclic ketones with diluted $H_2O_2$ with good activities and very high selectivity to the corresponding lactone.[463] When a double bond is also present in the reactant cyclic ketone, a very high chemoselectivity for the Baeyer−Villiger reaction is observed with Sn-Beta catalyst (Table 4).

The Sn located in the framework of Beta acts as a Lewis acid coordinating the ketone on the Sn atoms. For studying the reaction mechanism on this catalyst, methylcyclohexanone labeled with $^{18}O$ was reacted. The Baeyer−Villiger oxidation leads the incorporation of all labeled oxygen into the lactone product as carbonyl oxygen and none is present as ring oxygen. Thus, it was concluded that the Baeyer−Villiger oxidation with $H_2O_2$ on Sn-Beta proceeds via a "Criegee" adducts, where $H_2O_2$ adds to the ketone activated by the Sn-Beta, and the formation of dioxiranes or carbonyl oxides as intermediates can be excluded. The complete mechanistic cycle proposed is presented in Figure 4.

Sn-Beta also carries out the selective Baeyer−Villiger oxidation of aldehydes to carboxylic acids and shows the shape selectivity behavior associated to the pore diameter and internal void space of this zeolite.[476]

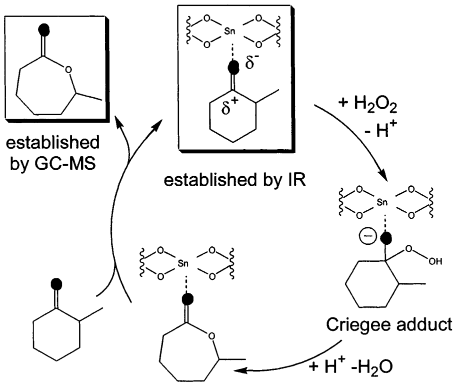
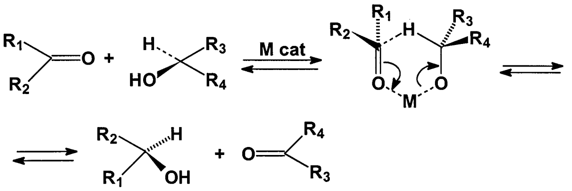


**Figure 4.** Mechanism of Baeyer–Villiger oxidation of 2-methyl-cyclohexanone catalyzed by Sn–Beta.

As reported earlier, the Oppenauer oxidation of alcohols by ketones is a very selective oxidation reaction when the molecule contains other groups susceptible to be oxidized. The opposite reaction, i.e., the reduction of carbonyl compounds by alcohols, is called the Meerwein–Ponndorf–Verley reaction. Both types of reactions proceed via a complex in which both reactants are coordinated to a Lewis acid metal ion and a hydride transfer from the alcohol to the carbonyl group occurs (Scheme 44)

**Scheme 44**



Usually, metal *tert*-butoxides Lewis acids are used in these oxidations, one of the most common being Al(OiPr)$_3$ and more recently other highly active aluminum alkoxides.[525] Therefore, molecular sieves containing Lewis acids should be appropriate catalysts for the Meerwein–Ponndorf–Verley–Oppenauer reactions. We have seen previously that Lewis acids can be generated in zeolites from the extraframework Al species (EFAL), from exchanged cations, and by framework isomorphous substitutions. It is not surprising then that A, X, and Y zeolites exchanged or impregnated with alkali or alkaline earth cations have been used as catalyst for Meerwein–Ponndorf–Verley and Oppenauer reactions in gas phase.[526–528] More interesting zeolite catalysts in the liquid-phase turned to be Al-Beta and Ti-Beta zeolites. The Meerwein–Ponndorf–Verley reduction of 4-*tert*-butylcyclohexanone to 4-*tert*-butylcyclohexanol, a classical transformation for this reaction type, can be catalyzed by Al-Beta and Ti-Beta zeolites. The high selectivity toward the thermodynamically less favored cis-alcohol was explained by zeolite shape selectivity, while the active sites were the extraframework aluminum and framework Ti.[529–531] In the case of Ti-Beta, the activity of the catalyst in the gas-phase reaction was found to correlate with the reduction potential of the alcohol, i.e., secondary alcohols are more active than primary alcohols. The selectivity was dependent on the polarity of the alcohol and the zeolite. An advantage of Ti-Beta in the gas-phase Meerwein–Ponndorf–Verley and Oppenauer reactions is the high resistance to water and ammonia and the excellent stability.[370] Beta zeolite with a large amount of extraframework aluminum acting as strong Lewis acids was very active as a Meerwein–Ponndorf–Verley and Oppenauer catalyst, but the selectivity was somewhat lower due to the presence of residual Brönsted acidity.

Very recently, Sn-Beta has been introduced as a Meerwein–Ponndorf–Verley and Oppenauer catalyst, based on the fact that it has a stronger Lewis acidity than Ti-Beta, but has not residual Brönsted acidity as it was the case of Al-Beta. The Sn-Beta zeolite allows one to work at low ratios alcohol/ketone and it gives higher activity and selectivity than either Ti-Beta or Al-Beta.[476] It is interesting to notice that the Sn-Beta catalyst has been active and selective for oxidizing vainilline alcohol to vainilline by means of the Meerwein–Ponndorf–Verley and Oppenauer reaction.[532]

Very recently, the enantioselective synthesis of chiral alcohols by the Meerwein–Ponndorf–Verley and Oppenauer reduction of the corresponding ketone has been achieved by a ruthenium complex of *N*-benzyl-(1*R*,2*R*)-(−)-norephedrine covalently tethered to silica. The ee was as high as 90% at 95% conversion.[533] This report could trigger research aimed at developing solid catalysts for enantioselective Meerwein–Ponndorf–Verley–Oppenauer reaction.

It appears to us that both micro and mesoporous substituted molecular sieves can be promising heterogeneous catalysts for the Meerwein–Ponndorf–Verley and Oppenauer reactions provided that Lewis acidity and solid polarity can be adjusted to the requirements of a particular reaction. These polarity adjustments can be quite useful to control reactant concentrations within the pores and in this way to be able to work with reactant concentrations in the reaction media more adequate for industrial applications. Furthermore, the use of chiral auxiliaries, chiral ligands, and ship-in-a-bottle chiral complexes remain a field to be explored in more detail using molecular sieves as catalysts for Meerwein–Ponndorf–Verley and Oppenauer reactions.

### *12. Selective Oxidations Using $N_2O$.*

Dehydroxylated and high-silica pentasil HZSM-5 zeolites have been used as catalysts for the selective oxidation of aromatic compounds including benzene, chlorobenzene, difluorobenzenes, phenol, styrene, and alkylbenzenes into their corresponding phenols using nitrous oxide as oxidant.[534,535] Steamed H/AlZSM-5 with strong Lewis acid sites is highly active for the oxidation of benzene with $N_2O$.[75] High phenol yields (70–80% in the case of hydroxylation of benzene), high selectivities and regioselectivities were observed in all cases. The active sites were shown to be strong Lewis acid–base pair sites formed upon dehydroxylation of acidic HZSM-5 zeolite.[75,534]

Likewise, metal-containing zeolites have also been active for the hydroxylation of benzene using $N_2O$ as oxidant. Yields up to 16% with 99% selectively can be achieved at 400 °C of reaction temperature.[536,537]

The catalytic performance of the zeolite can be improved by incorporating small iron amounts into zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-23, mordenite, Beta, EU-1. Phenol yields of 20−30% with selectivities 90−97% have been achieved using iron-doped zeolites.[538,539] An optimal content and distribution of extraframework iron in Fe-silicates increases phenol selectivity, while high acidity increases benzene conversion, but lowers phenol yield. It has been observed that Lewis acids caused catalyst deactivation.[540] Even at low temperatures, $N_2O$ does not adsorb as such on the catalyst but undergoes decomposition.[541] Apparently, the same sites are responsible for benzene oxidation and $N_2O$ decomposition.[540] Iron ions can be incorporated into the zeolite either during the synthesis or by some postsynthesis technique.[542] Considering a general composition of the catalyst: $y$ $El_2O_3$: $x$ $Fe_2O_3$: $SiO_2$ in which $y = 0-6.5 \times 10^{-2}$ and $x = 1.5 \times 10^{-5} - 2 \times 10^{-2}$, the incorporation of elements (El) in the general composition of the 2, 3, 4, and 5 periods of the periodic system has been reported.[538] Aluminum-containing zeolites are more active, while the introduction of $Na^+$ in the zeolite decreases the catalyst activity.[538] Inert gas additive has been used to prevent reactor temperature increase due to the exothermicity of the reaction. However, in all cases catalyst deactivation with time on stream is one of the main obstacles for process commercialization.

Catalyst stability can be increased by hydrothermal treatment of the zeolite.[539,543] Key parameters for steam treatment are temperature, steam partial pressure, and time of treatment. It has been reported that a hydrothermal treatment at 700 °C with 50% molar $H_2O$ for 2 h increases benzene conversion and catalyst stability when using ZSM-5.[539] However, the optimal conditions of hydrothermal activation can be different for different types of catalysts. A further improvement in catalyst stability for benzene hydroxylation has been achieved by acid treatment of the zeolite after hydrothermal treatment.[544] Hydrothermal treatment of the catalyst is believed to remove aluminum from the framework of the zeolite but not from the bulk of the zeolite material.

### 13. Selective Oxidations Using Molecular Oxygen

There are some important unresolved selective oxidations that have been attempted using molecular sieve catalysts. Among them the oxyfunctionalization of alkanes and cycloalkanes is of particular importance.

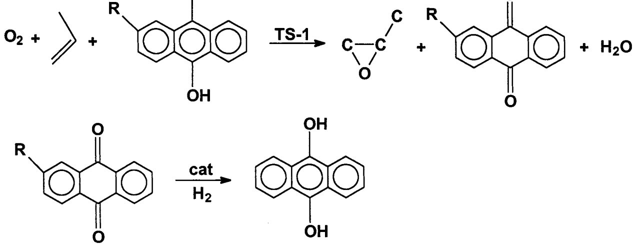
Alkane oxidation with dioxygen through a radical mechanism is generally referred to as autoxidation and suffers from the relatively harsh conditions to be initiated and very low selectivity, due to secondary reactions of the primary products.

Although there have been major advances in the oxidation of saturated hydrocarbons with molecular oxygen, the development of effective and selective methods for the catalytic functionalization of hydrocarbons still remains a major challenge in oxidation chemistry.[276,277,545−551] It seems that alkane activation on a solid surface requires the presence of strong acid or basic sites.[481,552] In the following section, we will present some recent progress in the application of solid Lewis acids as catalysts using oxygen as oxidizing reagent.

**a. Molecular Sieves as Catalysts.** Enzymes such as cytochrome P-450 and non-heme, iron-based oxidase are able to carry out selectively the oxyfunctionalization of alkanes with $O_2$. On the other hand, inorganic catalysts such as transition metal complexes and metal substituted polyoxometalates either in homogeneous phase or supported on a solid carrier by anchoring in mesoporous materials or by encapsulation in microporous molecular sieves are effective when using oxidants such as iodosylbenzene, alkyl hydroperoxides, and hydrogen peroxide,[283,284,553−558] and can, in some cases, also use molecular oxygen as oxidant.[559−562]

Aldehydes are oxidized to the corresponding peracids using $O_2$. When this is done in the presence of a reactant able to be oxidized by the peracids, a system is developed in which the aldehyde can act as a oxygen transfer agent. This process can be carried out in homogeneous phase (Mukaiyama system),[563,564] and has also been carried out using aluminophosphates containing Mn (III) and Co (III) at 323 K and 30 bar and using benzaldehyde as the oxidant transfer agent to epoxidize cyclohexene, α-pinene, limonene, styrene, and 1-hexene,[565] as well as to carry out Baeyer−Villiger oxidations.[566] The limitation of this procedure is that a sacrificial reactant, in this case benzaldehyde, is used that is transformed into benzoic acid. From this point of view, it is much better to use either $H_2O_2$ or $H_2O_2$ generated in situ. Thus, in an analogous way, $H_2O_2$ could also be generated in situ in the reaction media, and then it acts as the oxidant in the presence of the adequate catalyst. Thus, Solvay describes a process for the production of $H_2O_2$ using Pd on alumina catalyzed hydrogenation in an organic solvent in the presence of an alkylanthraquinone followed by oxidation in air. They also reported that organic peracids were efficiently prepared from the corresponding acid and $H_2O_2$ through the use of a support metal oxide that has been silanized.[567,568] Thus, Clerici and Ingallina [332,569] were able to epoxidize propylene in the presence of TS-1 and in one pot starting with an alkylated anthrahydroquinone with molecular oxygen and propylene (Scheme 45).

**Scheme 45**



In this process, the organic carrier does not interfere in the catalytic process since it cannot penetrate into the zeolite pores. In this process, it is claimed that the solvent and anthraquinone derivative play a crucial role. Yields of propylene, based on starting alkyl anthrahydroquinone, of 78% are obtained. Anthrahydroquinone is consumed in the first process, but regenerated separately by subsequent hydrogenation.

A similar reaction cycle is claimed by ARCO to occur with tetra-alkylammonium salts of the anthraquinone-2,6-disulfonic acid in aqueous methanol, giving good yields of propylene epoxide.[570]

Following the methodology of generating $H_2O_2$ in situ, the most direct way to make this would be using $O_2$ and $H_2$. This is done by carrying out the propylene epoxidation on a bifunctional catalyst formed by Pd and Pt on TS-1. The noble metal catalyzes the formation of $H_2O_2$ from $H_2$ and $O_2$, while the TS-1 will react the formed $H_2O_2$ with propylene to give the epoxide. An optimized catalyst gives propylene oxide with selectivities up to 85% at conversions between 15 and 20%.[75] Two drawbacks of this process is the need to operate under conditions close to the explosion limit, and the formation of propane coming from hydrogenation of propylene.

It is interesting to point out that when a catalyst formed by gold dispersed on TS-1 is used to epoxidize propylene with $H_2O_2$ formed in situ by reacting $H_2$ and $O_2$ at low temperature, no propane is formed and the selectivity to epoxide is high (99%), but conversion is low (<2%).[571] There is no doubt that this system deserves further work trying to find the reasons for the low conversion obtained.

Transition metal substituted molecular sieves have also been used as selective catalysts for oxidizing saturated hydrocarbons using molecular oxygen. For instance, V-containing silicalite showed activity and selectivity for the oxidative dehydrogenation of lower alkanes. In this sense, Zatorski et al.[572] have carried out selectively the oxidative dehydrogenation of propane to propene with $O_2$ and $N_2O$. The success of vanadium silicalite for the above reaction is attributed to the presence of vanadium (V) as the sole site of oxygen activation together with the absence of Brönsted acidity and a limited tendency for oxygen insertion or alkene activation at allylic positions due to the presence of stable V−O−Si bonds containing nonelectrophilic bridging oxygen ions, and a stable coordination of vanadium.[573]

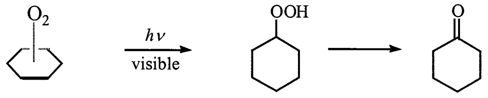
Transition metals such as $Cr^{3+}$, $Co^{III}$, $Mn^{III}$, $Fe^{III}$ substituted in molecular sieve AlPO type structures could, in principle, in the presence of oxygen and saturated hydrocarbons favor the production of the free radicals involved in the oxyfunctionalization process. The existence of a radical mechanism for the oxidation of saturated hydrocarbons using transition metals substituted AlPOs has been demonstrated by observing not only the reaction induction period and the diminishing of this when small amounts of a free radical initiator (TBHP) are added, but also by the reaction inhibitor effect of the well-known free radical scavenger hydroquinone.[574,575] Indeed, chromium substituted aluminophosphate-5 (CrAPO-5) was active for the liquid-phase autoxidation of cyclohexane to cyclohexanone with $O_2$, in the presence of small amounts of alkyl hydroperoxide initiator. Tetralin, indone, and ethylbenzene have also been converted to the corresponding ketones.[452,454,574]

Unfortunately, the system is not fully heterogeneous due to some leaching of $Cr^{3+}$ occurring during the reaction. Similarly, the use of acetic acid solvent during the aerobic oxidation of cyclohexane to adipic acid using CoAPO-5 results in leaching of cobalt, being the leached cobalt responsible for the catalytic activity.[576] There is an interesting study on CoAPO-5 showing that in the presence of a strong apolar solvent, only an extremely low amount of Co is leached at conversion levels below 10% that cannot explain the autoxidation activity.[523] When conversion level increases the acids formed in consecutive reactions enhances considerably Co leaching.

The interest of cyclohexane oxidation to produce cyclohexanone (for production of ϵ-caprolactam) and adipic acid (for producing polyamide fibers and polyurethane resins) strongly justify further efforts in looking for a selective heterogeneous catalyst for cyclohexane autoxidation. Recently, MnAPO-18 and MnAPO-36 have been reported to be stable catalysts for the autoxidation of cyclohexane when using the substrate as solvent.[577,578] In this case, the influence of the level of conversion on leaching should also be carefully addressed.

A novel concept and very promising system to effect the oxidation of alkanes and unsaturated hydrocarbons consists of taking advantage of the electrostatic fields experienced inside the zeolite supercages, particularly those ion-exchanged with alkaline-earth cations, to stablize the collisional charge-transfer complexes between molecular oxygen and alkanes, alkenes, and aromatic hydrocarbons.[579−585] The hydrocarbon oxygen complexes undergoes a considerable stabilization (up to 8 kcal/mol). This stabilization can be experimentally demonstrated by measuring in the UV−Vis spectrum the $\lambda_{max}$ of the corresponding CT complexes and observing a gradual shift toward longer wavelengths as the Coulombic fields inside the zeolite cages increase. By selective excitation of these CT complexes with visible red light, the corresponding hydroperoxides are formed with almost complete selectivity. The course of the irradiation can be followed and the reaction intermediates characterized by in situ FT-IR spectroscopy of zeolite wafers in which the hydrocarbon and oxygen have been coadsorbed from the vapor phase. In this way, cyclohexane can be oxidized by oxygen to cyclohexane hydroperoxide with an almost complete selectivity at very high cyclohexane conversion. The proposed reaction mechanism is indicated in Scheme 46 and is thought to involve and initial electron transfer within the alkane−oxygen complex followed by hydrogen abstraction with the formation in a cage of a geminate carbon centered radical and a hydroperoxyl radical. This radical pair readily recombines to the alkylhydroperoxide. In this hydrocarbon selective oxidation, the zeolite plays a “passive” role merely defining a highly polar reaction cavity in which the CT complex becomes stabilized. Clearly, it would be worth explor-

**Scheme 46**



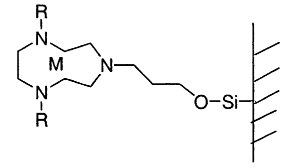
ing the promising opportunities of this remarkable stabilization of the contact charge transfer complex in continuous flow operation. Also, the development of the thermal version of this originally photochemical reaction will be of large interest due to the problem of reactor design using light as reagent and the economy of the process.[586]

Following with catalytic photochemical irradiation to oxidize alkanes, it has been established that the IR photolysis of alkanes on the surface of a solid can also promote their oxidation. Thus, laser stimulated isobutane selective oxidation to methacrylic acid over mixed lithium, lead phosphate has been reported.[587] For samples containing 5% $Li_3PO_4$, surface characterization indicates that the main crystal phase exposed to isobutane is $Pb_3(PO_4)_2$ in which $Li_3PO_4$ is dispersed like in molecular state. Lewis basic sites are oxygens of the P=O and P−O−P groups, and Lewis acid sites are $Pb^{2+}$ and $Li^+$. The two terminal methyl groups are supposed to be chemisorbed on the terminal oxygen of neighboring Lewis basic sites. Laser photons at 1048 $cm^{-1}$ in the IR region excited the P=O bonds and after 1000 laser pulses the conversion of isobutane is about 8.2%. The product distribution is isobutene, methacrylic alcohol, and methacrylic acid, the selectivity to the latter exceeding 66%.[587]

Analogously, methanol undergoes IR laser-stimulated oxidative coupling to ethylene glycol on solid $Li_3PO_4$, $FePO_4$, and $Li_3PO_4$ (5%)/$FePO_4$.[588,589] Spectroscopic and desorption techniques support that there are two kinds of methanol adsorption on the surface of these phosphates. Adsorption through the interaction of C−H on P=O groups of the catalyst and dissociative adsorption of $^{\bullet}CH_2{-}OH$ radicals on Lewis acid sites located on metal ions. Then, selective excitation of the solid surface P=O bonds using a IR 1077 $cm^{-1}$ laser pulse causes the vibrational activation of the surface lattice oxygen which on reaction with adsorbed $CH_3OH$ leads to hydrogen atom abstraction forming $^{\bullet}CH_2OH$ and enhancing of the oxidative coupling to ethylene glycol.[588,589] The increase in the reaction temperature promotes product desorption, but also thermal reactions with formation of byproducts such as dimethyl ether, formaldehyde, and ethylene. Given the higher penetration power of IR radiation on solids, it would be of much interest to expand and explore the possibility to apply IR irradiation to promote alkane oxidation and other types of catalytic reactions.

A heterogeneous cobalt catalyst based on an immobilized trimeric cobalt complex on MCM-41 has been claimed for the conversion of cyclohexane to cyclohexanol and cyclohexanone in an aerobic system using the substrate as solvent. The turnover numbers are modest (∼2 mol/site/h). Again leaching may be an issue when adipic acid will be formed at higher conversion levels.

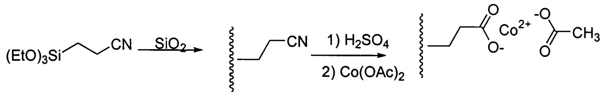
An active epoxidation catalyst based on silica and MCM-supported metal complexes with the triazacyclononane ligand system has been prepared.[590] One of the N atoms is covalently linked to the silica wall through a glycidyl or chloropropyl linker. The other two N atoms were reacted with propylene oxide. Using the epoxidation of styrene as a test reaction, it was found the selectivities and turnover numbers are higher for MCM-derived materials than for silica.[590]



triazacyclononane anchored on MCM

Liquid-phase partial oxidation of alkyl aromatic compounds by air at atmospheric pressure has been conducted in the presence of chemically modified mesoporous silica containing chromium ions strongly coordinated to a carboxylate group covalently attached to the silica surface.[591] The preparation procedure is indicated in Scheme 47. This solid catalyst can effect the oxidation of neat ethylbenzene in air at reflux temperature with an isolated acetophenone yield of 50%. The catalyst was reused twice without any regeneration or conditioning treatment, by simply decanting the liquid from the reactor and adding fresh substrate. No leaching of the chromium was observed. The same catalyst also performs successfully for *p*-chlorotoluene and *p*-xylene.[591] It was claimed that the activity of this mesoporous silica-supported chromium catalyst is significantly higher than the commercially supported chromium catalyst.

**Scheme 47**



In the case of *n*-alkane oxyfunctionalization, oxidation at low temperatures and at the terminal carbon is highly preferred. A recent work has showed that Co and MnAlPO-18 is a regioselective oxidation catalyst for *n*-alkanes. Because of the end-on approach of the *n*-paraffin in ALPO-18, owing to the pore dimensions and topology of this molecular sieve, only the $C_1$ and $C_2$ positions are preferentially oxidized. When other structures with larger pore dimensions (AlPO-36 and AlPO-5) are used, oxyfunctionalization is predominant at the $C_3$ and $C_4$ positions.[301]

**b. Catalyst for Epoxidation of Propylene.** The oxidation of olefins by molecular oxygen was applied commercially to ethylene, but oxygen epoxidation for larger olefins has been mostly unsuccessful using transition metal substituted molecular sieves as catalysts. The failure to directly epoxidize allylic olefins to their corresponding epoxides, and more specifically the case of propylene, can be related to the fact that the bond dissociation energy of the allylic C−H bond in propylene is 77 kcal $mol^{-1}$ much smaller than the corresponding dissociation energy of the vinylic C−H bond in ethylene that is 112 kcal $mol^{-1}$.[592] Then, abstraction of the allylic C−H bond by $O_2$ in propylene is considerably favored compared to the case of ethylene and consequently the selectivity to the epoxide is lower.

A large effort has been done for the development of soluble metal and metal complexes able to oxidize long chain olefins in liquid phase using $O_2$ as a direct oxidant. In general it can be said that the most important limitations for the use of liquid-phase olefin epoxidation using solid catalysts are the low rates and low turnover frequencies, together with the too low selectivity to the desired epoxide owing to the presence of less desired free radical chain reactions.[593]

Molten salt mixtures of $LiNO_3$, $NaNO_3$ have been used for epoxidation of propylene with $O_2$ in vapor phase. However, it is not proven that molten salts apart from being the solvent act as catalysts. It is believed that the reaction is mainly thermal while some of the propylene oxide can also be produced from the co-oxidation of $C_3H_6$ by the peracids formed as subproducts in the thermal process.

We have discussed above about the indirect way of using $O_2$ as an oxidant to generate in situ $H_2O_2$ and using Ti-containing molecular sieves, as catalysts. Besides these interesting results, it has been recently described a non-molecular sieve oxidation catalysts formed by gold supported on $TiO_2$.[594,595] This catalyst is able to generate "in situ" $H_2O_2$ and then to oxidize propylene to epoxide when a reactant mixture of propylene, $O_2$, and $H_2$ is used. An important catalyst characteristic is that Au particles must have a hemispherically shape with sizes between 2.0 and 4.0 nm in diameter. The formation of small Au particles on the surface of $TiO_2$ is achieved by deposition−precipitation of $Au(OH)_3$, starting from a basic solution of chloriauric acid at pH = 7−10. After washing the sample, the catalyst is calcined at 400 °C to form the gold particles.

The catalyst active sites are believed to be Ti−Au bridged sites that would form the activated molecular oxygen species. Reaction with $H_2$ forms the hydroperoxo species that will be responsible for the epoxidation of propylene.[332] This mechanism implies that the active sites for the reaction must exist at the interfacial edge of the hemispherical Au particles and the $TiO_2$ support. This, indeed, would be consistent with the observation that the activity of an Au-supported $TiO_2$ catalyst is higher than that of Au/TS-1 at the same Au weight loadings and crystallite size.[571]

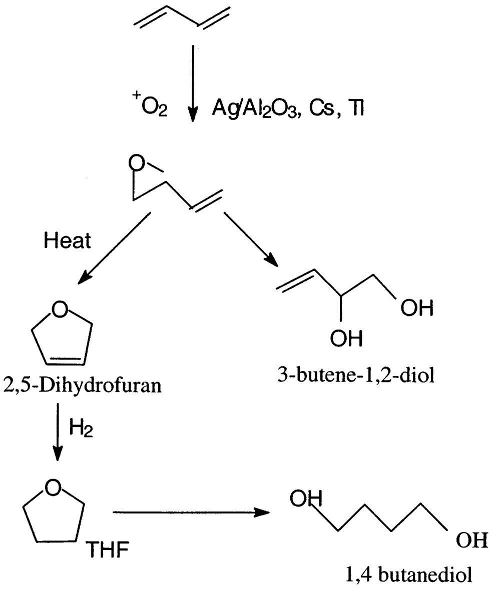
Despite the high selectivities to propylene oxide obtained with the Au/$TiO_2$ system, conversions are low, and turnover frequencies with this system for propylene epoxidation are on the order of 20−200 times lower than for the epoxidation of ethylene with silver catalysts. An additional drawback of the Au/$TiO_2$ catalyst is deactivation. Nevertheless, a considerable effort is currently being devoted to improve catalyst life and activity by means of modifying the Ti-containing support and catalyst preparation procedures.[596−599]

Direct epoxidation of propylene with $O_2$ has been carried out using silver catalysts. If the silver ethylene oxidation catalyst is used directly for the epoxidation of propylene very poor results are obtained. However, activity and selectivity improve when silver powder is slurred with group IIA metal halides, or when silver is combined with $K^+$ and $CaCO_3$.[600−603]

Promising catalytic systems based on the above ideas have been described by Gaffney et al.[604−608] These systems use silver catalyst modified by K, Cl, Mo, Re, W as promoters and $CaCO_3$, together with the introduction in the reactor of chlorine (in the form of ethyl chloride, up to 500 ppm) and up to 500 ppm of NO. With this catalytic system, 3.2% conversion levels with 59% selectivity to propylene oxide are achieved, the yield being not high enough for commercial application. The activity of the above catalyst has been explained by the authors assuming selective sites at the interface of Ag and $CaCO_3$. If this is so, then the introduction of high levels of K and Cl that are responsible for increasing catalyst selectivity may be due to the selective poisoning of the less selective Ag sites at the surface of the silver surface in benefit of the desirable, more selective Ag sites at the interface of silver and $CaCO_3$. If this hypothesis is true, increasing the surface contact between silver and $CaCO_3$ should result in an increase of the active and selective sites and therefore in an increase in propylene yield.

Silver on alumina modified with Cs or Tl is a selective catalyst for the epoxidation of higher olefins that do not contain reactive allylic hydrogen atoms.[609−616] This catalyst was specially useful in the epoxidation of 1,4-butadiene (Scheme 48). The epoxidation of butadiene results in a selectivity to 1,2-epoxybutene of 95% with conversions close to 13%.

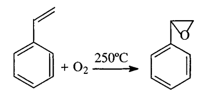
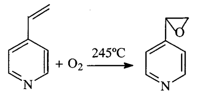
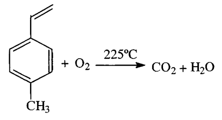
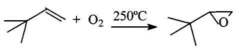
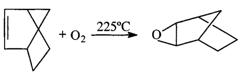
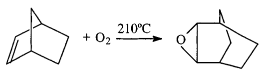
**Scheme 48**



The process uses a lower hydrocarbon as an inert co-feed that lowers the reaction temperature from 220 to 200 °C. This process is commercially used today.

Besides butadiene, Monnier[610] has reported the selective epoxidation of other higher nonallylic olefins as the ones summarized in Table 5 using CsI, CsCl, and RbCl promoted Ag/$Al_2O_3$ silver on alumina catalysts.

**Table 5. Epoxidation of Olefins with CsCl Promoted $Ag/Al_2O_3$ Catalysts**[a]

| REACTION | Molar Selectivity (%) | Conversion (%) |
|---|---|---|
|  | 95 | 19 |
|  | 95 | 21 |
|  | 0 | 100 |
|  | 95 | 1.5 |
|  | 92 | 43 |
|  | 36 | 4 |

[a] Taken from ref 610.

**Table 6. Product Distribution for the Ethane/Ethylene Oxidation by $O_2$ at 500 °C, and 400 psi in the Presence of $Mo_{0.37}Re_{0.25}V_{0.26}Nb_{0.7}Sb_{0.03}Ca_{0.02}O_x$**[a]

| product | selectivity/mol % |
|---|---|
| acetic acid | 88.9 |
| ethanol | 0.2 |
| ethyl acetate | 0.2 |
| carbon dioxide | 7.2 |
| carbon monoxide | 3.5 |

[a] Taken from ref 625.

This catalytic system offers great potential and deserves further studies to determine which are the active sites and then to introduce rational catalyst modifications trying to increase their turnover number, activity, and selectivity.

**c. Oxidation of Ethane and Ethylene.** A catalytic process for the direct oxidation of ethylene to acetic acid started commercially in 1997.[617−619] In this context, a metal catalyst with the composition $TiPd_{0.01}K_{0.03}PO_x$ has been claimed to convert a mixture of ethylene and air at 205 °C and 180 psi to acetic acid in 72.8% and ethylene glycol. Analogously, propylene was oxidized to acetone and propylene glycol using the same catalyst.[620,621]

Ethane can also be directly oxidized to acetic acid using $Re_{0.117}VO_{0.254}Nb_{0.067}Sb_{0.03}K_{0.05}$, $Mo_{56}Re_6V_{26}Nb_7Sb_3Ca_2$, a titania modified V−P−O catalyst, or a metal modified V−P−O catalysts.[622−625] A recent process gives high conversions and yields of acetic acid with a feed composed by 2% ethylene−98% ethane in a fluidized bed of $Mo_{0.37}Re_{0.25}V_{0.26}Nb_{0.7}Sb_{0.03}Ca_{0.02}O_x$ using a gas recycle to obtain at 500 °C and 400 psi, high selectivities at ethane/ethylene conversion of 97% (Table 6).

It is interesting to point out that despite the extensive and excellent work carried out by BP on the production of acetic acid using solid catalysts, it was announced that they are commercially introducing an Ir carbonylation catalyst called CATIVA.

Catalytic oxidation of paraffins and olefins to products such as maleic anhydride, methacrylic acid, acrolein and acrylic acid, and acrylonitrile is a very active area of research and it has been discussed in part when commenting on the vanadium-containing catalysts.

## IV. Application of Lewis Acid Catalyzed Oxidations in Various Fields

### A. Examples of Catalytic Oxidations with Lewis Acids in Biochemistry

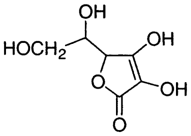
Lewis acid catalyzed oxidations have also a wide occurrence in biochemistry. Cellular oxidative stress has recently attracted considerable interest since it has been blamed, among other effects, as one of the main factors responsible for aging. The biomolecules involved in the oxidative stress, the transformations that they undergo, and the natural protecting mechanisms are the main aspects recently investigated related to catalytic oxidation. Also relevant to this review are those enzymatic systems that catalyze biochemical oxidations. Given the extension of these topics, only some pertinent contributions will be covered.

Transition metals in trace amounts have been found to be responsible for the oxidation of some biomolecules. Biomolecules can be damaged by oxidation and lose their function. A water-soluble salen Mn(III) or Ni(II) complex can act as efficient catalyst for the oxidative cleavage of DNA by magnesium monoperoxyphthalate at concentrations as low as 1 $\mu$M.[626] In contrast, other metal complexes do not induce any significant DNA damage at micromolar concentrations.[626]

It can be a metal ion interaction in the oxidative stress process. Thus, $Zn^{2+}$ ions acts as inhibitors of the $Cu^{2+}$ and $Fe^{2+}$-initiated lipid oxidation, but do not prevent other oxidation processes that are promoted by other initiators such as azo compounds, UV irradiation, superoxide, or peroxinitrite.[627] The presence of $Zn^{2+}$ does not change the physical properties of bilipidic membranes, but its mechanism of oxidation inhibition is related to its binding to the negative sites of the bilipidic membranes preventing $Cu^{2+}$ and $Fe^{2+}$ in occupying these negative positions on the membrane.[627]

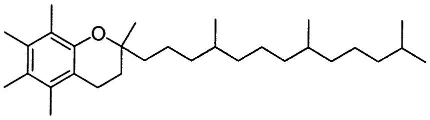
The previous examples demonstrate that appropriate analytical techniques are necessary to quantify metal ions at low concentrations. In the context of assessing the presence of trace metal concentrations with, however, catalytic activity, it has been proposed that the lack of occurrence of ascorbate (vitamin C) autoxidation in aerated aqueous solutions at neutral pH is a test reaction to assess the total absence of transition metal ions in aqueous buffer solutions for biomedical applications. Vitamin C is an important water-soluble natural antioxidant. It was found that in metal-free, air-saturated aqueous solutions, the first-order rate constant of ascorbate disappearance at pH 7 has to be lower than $6 \times 10^{-7}$ $s^{-1}$.[628]

Acceleration of ascorbate oxidation indicates the presence of transition metals even in trace amounts.[629]



ascorbic acid

In a parallel way to ascorbic acid, α-tocopherol (vitamin E) is the most important lipid soluble antioxidant in human plasma. However, α-tocopherol has been found to promote oxidation of lipoproteins as it was demonstrated by the transformation of cholesteryl esters into their hydroperoxides.[630] In vitro and in vivo α-tocopherol-depleted lipoproteins and plasma lipids were highly resistant to hydroxyl and peroxyl radicals peroxidation at mild radical flux. Wherever tested (in vivo or in vitro), the oxidability of low-density lipoproteins increases with α-tocopherol content. However, under high fluxes of ROO$^•$ and $^•$OH, the influence α-tocopherol changes from pro- to antioxidant, with the switching point for $^•$OH being lower than for ROO$^•$.[630]



α-tocopherol

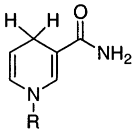
Highly reactive radicals (such as $^•$OH) promote oxidative stress in biomolecules under aerobic conditions. The oxidative stress is initiated by hydrogen abstraction or even electron transfer from an electron-rich moiety of the biomolecule to the aggressive radical. Hydroxyl radicals can be formed in solutions containing oxygen or hydrogen peroxide when trace transition metals are present. From there, it derives the importance to determine the presence of peroxides in biochemical fluids. A procedure developed for the detection of hydrogen peroxide in biological fluids involves contacting the solution with a redox indicator and an iron metal complex of creatinine or guanidine.[631]

Amino acids of peptides and proteins can undergo irreversible modification, activity loss, and increased susceptibility to proteolysis and fragmentation initiated by hydroxyl radicals generated from hydrogen peroxide in the presence of metals. For instance, it has been reported that histidine amino acid undergoes very easily a chemical degradation by hydroxyl radicals.[632]

Related with the understanding of amyloid $\beta$ deposits that appear in Alzheimer and mad cow diseases, it was reported that these amyloids were able to generate free radicals detectable by conventional ESR spectroscopy. It was even proposed that these radicals produce the neurotoxicity manifested in these diseases. Subsequent studies, however, have shown that these radicals are indeed formed by traces of transition metals present as impurities in the commercial di-*N*-*tert*-butyl-α-phenylnitrone reagent used as the ESR detectable radical source.[633]

There is one type of liquid chromatography to separate biomolecules based on metal affinity. In this chromatography, the stationary phase contains an immobilized transition metal complex that interacts with the biomolecule. Using lactate dehydrogenase as a probe enzyme, it was demonstrated that liquid chromatography based on a metal affinity column using immobilized $Cu^{2+}$-iminodiacetic acid may produce the partial or total inactivation of a enzyme when oxygen, hydrogen peroxide, or reducing agents such as ascorbate are present in the eluate. In the absence of redox reagents, no decrease in the enzymatic activity of lactate dehydrogenase was observed. The results show that one has to be aware of the possibility that this type of liquid chromatography alters a biomolecule during the purification process.[634]

Magnesium can act as Lewis acid and through binding with a carbonyl group can control the stereochemistry of the oxidation of NADH analogues by *p*-benzoquinones.[635] The axis of the carbonyl group bound to the dihydropyridine heterocycle forms a dihedral angle of 55°. Without $Mg^{2+}$ ion, the anti hydrogen with respect to the carbonyl group is 3 to 30 times much more reactive than the corresponding syn hydrogen. In contrast, when $Mg^{2+}$ binds to the carbonyl group the selectivity is shifted toward syn preference.[635] This is a good example of Lewis acid assisted oxidation in which the product stereoselectivity is controlled by the Lewis acid interaction with a remote group.



redox active part of NADH

Frequently, enzymes have an active center surrounded by a proteinic backbone that modulates the activity of the center and defines the reaction cavity in which the transformation is going to occur. In many aspects, this situation is similar to that occurring in some porous solid catalysts, in which the active site is embedded in the interior of a rigid matrix. In some way, enzymes have inspired some advances in heterogeneous catalysis.[636−639]

Manganese is an essential bioelement that is present in the active site of a large number of enzymes, such as citochromes. In this case, the enzyme contains a manganese complex with a porphyrin ligand. It is widely accepted that manganese plays two functional roles.[640] $Mn^{2+}$ acts as Lewis acid like other divalent ions such as $Mg^{2+}$, $Ca^{2+}$, or $Zn^{2+}$ like in arginase, glutamine synthase, phosphoenolpyruvate carboxykinase, malate synthase, and pyruvate carboxylase. On the other hand, at higher oxidation states ($Mn^{3+}$ or $Mn^{IV}$), manganese acts as oxidation site, like copper, iron, or cobalt. The most well-known enzymes of this type are manganese superoxide dismutase, manganese peroxidase, and manganese catalase. The last enzyme is responsible for one of the most important reactions occurring in green plants, namely, the light driven oxidation of water to oxygen and protons.[640]

A study on the role of non-heme iron cluster present on the flavoprotein 4-hydroxybutyryl-CoA deshydratase has shown that this enzyme contains a flavin FAD unit that undergoes reversible reduction/reoxidation during the catalytic cycle, but there was not equilibration with the non-heme [4Fe-4S] cluster, iron being difficult to reduce as assessed by EPR spectroscopy.[641] Apparently, the iron cluster serves as a Lewis acid site facilitating the oxidation process by interaction with the substrate.[641]

## B. Contribution of Permanganate to Green Chemistry

Permanganate has been the most popular oxidant whose reactions are studied in general organic chemistry textbooks,[151] and its chemistry has a long and extensive story. Permanganate is frequently proposed as the prototypical stoichiometric oxidant giving metal ion or oxide products for which green chemistry is searching replacement using catalytic oxidations. The main problem of the use of permanganate arises from the need of stoichiometric amounts and the production of large amounts of metal byproducts, rather than from its toxicity. Indeed, recycling of manganese dioxide, by reducing the product in basic media can help to circumvent the problem of wastes making the use of permanganate more environmentally attractive for industrial applications.[642] In this way, there is a process in which after the use of $KMnO_4$, the reduced $Mn^{2+}$ and other manganese species are separated by adsorption on diatomite, decalite, or fuller's earth.[643] Subsequent treatment of the material retained in the filter with 1.5−2.5 M nitric acid solution solubilizes the $K_2O$ and transforms the Mn species into $\gamma$-$MnO_2$ which is adequate to be used in dry cell batteries[643] or can be recycled. Alternatively, dissolved manganese from industrial water can be recovered using oxidizing agent such as $ClO_2$ or NaClO or even $KMnO_4$ to convert Mn ions into $MnO_2$ followed by microfiltration or ultrafiltration of the treated water.[644]

One aspect of green chemistry is pollution abatement. Permanganate can contribute to the development of green chemistry by helping to degrade pollutants.[645] In this context, potassium permanganate has been widely used in drinkable water treatment plants, although its use seems to decline. According to the American Water Works Association[646] up to 40% of the water plants used $KMnO_4$ for predisinfection/oxidation and organic removal, since it is effective to deal in potable waters with problems of iron, manganese, hydrogen sulfide, reservoir algae, and zebra mussels, while at the same time it improves the organoleptic properties of water in terms of color, odor, and taste.[646] In addition, $KMnO_4$ also produces the inactivation of bacteriophage and Legionella pneumophila. In a totally different aspect of water treatment, chemical oxygen demand is an important parameter to assess the organic content of a wastewater. Standard methods to determine such values are based on the $KMnO_4$ or $K_2Cr_2O_7$ oxidizability of wastewaters.[647]

Permanganate is a strong oxidant that has been used for the degradation of industrial pollutants and metal ions in effluents.[648−650] Thus, it is particularly suitable to oxidize phenols that are organic pollutants refractory to biological water remediation with bacteriae. Phenols are found in high concentration in industrial wastewaters from the petrochemical industry and paint stripping. Also, permanganate has been reported as a chemical oxidant for laboratory scale degradation of 1,1,2-trichloroethylene and perchloroethylene organic compounds present in contaminated soils and groundwater.[645] Dimethyl and diethyl sulfides in industrial wastewaters can be removed for deodorization by extraction with toluene and oxidation of the extracted sulfides with an aqueous solution of $KMnO_4$.[651] The organic solvent is separated from the aqueous solution in which oxidation has occurred and recycled.[651]

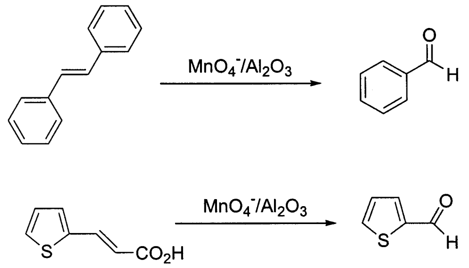
On a larger scale, potassium permanganate solutions have been injected into low-permeability, contaminated soils for in situ chemical oxidation of trichloroethene at a former industrial site.[652] After the treatment, the concentration of trichloroethene was below detection limit. However, the procedure suffers from an inhomogeneous distribution of $KMnO_4$ in the soil to achieve overall treatment performance.[652]

One of the industrial processes in which large quantities of oxidants are consumed is in the pulp and paper industry to remove lignin. Permanganate has been considered as a bleaching reagent for chlorine-free bleaching of kraft pulps.[653] Permanganate oxidizes lignin and is converted to $MnO_2$, which remains in the treated pulp fibers because of its insolubility in water.[653] Addition of oxalic acid as a reducing agent transforms $MnO_2$ into manganese ion after the pulp bleaching.[653] Using lignin models such as veratraldehyde, it was found that the pH of the bleaching liquor has to be kept over 2 to effectively degrade nonphenolic lignin.

A procedure to evaluate the quality of bitumens, petroleum resids, and asphaltics is based on the consumption of permanganate that is proportionally related to the content of structural elements.[654]

The wide interest of permanganate has promoted a series of studies to find effective ways of insolubilizing the oxidant allowing separation and reuse. In this way, it has been found that the activity and selectivity of permanganate can be modulated by adsorption on various solid supports.[655] In contrast to the products obtained when an inert support such as bentonite is used, permanganate adsorbed on moist alumina cleaves C−C bonds with the formation of aldehydes in good yields (70−95%) under mild conditions (Scheme 49). Apparently, the Lewis acidity of alumina participates in the proton-transfer steps that accompanies the oxidation reactions. Systematic studies on the specific reactivity of supported permanganate have, however, not been undertaken. Supported permanganate may be an interesting oxidant, provided that a recycling/reoxidation procedure is devised making possible its reuse.

**Scheme 49**



Highly toxic, volatile dimethylselenide can be completely transformed into nonpurgable dimethylselenoxide by reaction with $\delta$-$MnO_2$ which is converted into $Mn^{2+}$ ions.[656] Permanganate and chromate were found less efficient for this process. It is proposed that dimethylselenide acts as Lewis base and donates a lone electron pair to unoccupied orbitals of surface manganese atoms of $MnO_2$ that would act as Lewis acid site.[656]

Oxidative degradation of pyridine on the surface of hydrated manganese dioxide occurs through a two-step process. Fast adsorption of pyridine on the solid Lewis acid sites is followed by slower oxidation.[657] Autoclaving at about 150 °C for 2 days of a layered structure of Mn oxide obtained by reaction of $MnO_4^-$ and $Mn^{2+}$ in strong basic medium gives a thermally stable (500 °C) molecular sieve corresponding to natural todorokite, having 6.9 Å of pore diameter.[658] The solid exhibits Lewis and Brönsted acidity and has been proposed to have application as oxidation catalyst and as a sensor.[658] However, the porous structure of the Mn oxide collapses at 600 °C. Other porous manganese oxides having activity to oxidize alcohols to aldehydes or ketones have been recently reported.[659]

Selective oxidation of $NH_3$ by $NO_x$ operating at temperatures below 200 °C in the presence of water at $NO_x$ conversions higher than 80% at space velocities of 30000−50000 $h^{-1}$ have been reported with a $MnO_2$ catalyst prepared by egg-shell precipitation around NaY zeolite particles.[660]

## C. Catalytic Oxidations for Degradation of Pollutants

As we have been commenting on in the previous section, one important field in environmental science and technology is that devoted to pollution abatement and remediation of waste efluents. This field certainly will attrack more interest in the forthcoming years. A general methodology to treat wastes containing organic compounds is to perform a chemical oxidation of these effluents at the deepest possible degree of oxidation. Many of these processes are catalyzed by transition metals.

Although these catalytic oxidations are generally devised to degrade chemicals, transition metals may play a negative, unforeseen role in atmospheric pollution. In relation to acid rain and cloud acidity, it has been found that $SO_2$ oxidation by oxygen is catalyzed by aqueous Co, Cu, Mn, and Fe ions, this oxidation enhancing the damage of the acid rain.[661] The presence of simple carboxylic acid such as acetic, formic and oxalic acids inhibits this oxidation, an effect that was explained as reflecting the formation of Fe(III)-oxalate complex that leads to a depletion of catalytically active free Fe(III) cation.[662]

In this context, a hypothesis has been proposed in which the incomplete combustion of fossil fuels produces humic-like compounds that will form part of air particulates, conferring them the capacity to complex first-row transition metals. These complexes present in the air would participate in the production of free organic radicals by cycling these transition metals through two valence states.[663] Therefore, the concentration of transition metals and oxidizing power of air pollution particulates would increase with the content of humic-like substances associated to the pollution. This theory was supported by using filters to collect air-borne particulate and subsequently extracting the humic-like substances with alkali. There was a correlation between the concentration of metal in the particulate and the amount of humic-like present in the particulate. These analyses may explain the way in which substances derived from incomplete fuel combustion enhance the free radical ability of air particulate.[663]

On a more positive side of catalytic oxidations, aqueous solutions of transition metals have been used as catalysts in the remediation of polluted waters by promoting the oxidative degradation of the organic contaminants. Generally, the process requires the addition of a strong oxidizing reagent to produce a substantial degree of decomposition. Examples are the degradative oxidation of 4-aminopyridine by ozone in the presence of catalytic amounts of sulfates of V, Fe, or Cu[664] and the degradation of 1,4-dioxan as a model organic compound in water by ozone using first-row transition metal oxides as catalysts.[665] Cyanide is also oxidized to environmentally acceptable compounds by $H_2O_2$ with a heterogeneous catalyst containing Ag, Cu, or Ni on alumina, silica, or in a zeolite.[666]

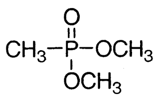
A procedure in which phenol, chlorinated phenols, and hydroquinolines are removed from wastewaters using high oxygen pressure and a large excess of alkali metal carbonates (typically over 20 mol of carbonate × mol of phenol) in the presence of a transition metal phthalocyanine, porphyrin, or salicylidene complex as catalyst has been reported.[667] In the absence of oxygen, a related treatment of phenol with transition metal-catalyzed has been reported to effect the formation of polyphenylene ethers.[668]

Polluting polyamine chelating agents can be removed from aqueous solutions by oxygen oxidation in the presence of equivalents amounts of transition metal ions followed by biological treatment with denitrifying and sulfate-reducing bacteria. The process can be completed by optional membrane filtration.[669]

Transition metals are also able to act as catalysts for the complete oxidation of volatile organic compounds.[670] $LaMnO^{3+}$ perovskite has shown activity for the total catalytic degradation of chlorinated $C_2$ hydrocarbons to $CO_x$, mainly $CO_2$, and HCl.[671] The presence of water has a positive effect on the degree of degradation, decreasing the amount of chlorinated byproducts and enhancing carbon dioxide formation.[671] Oxygen must also be present in the system to maintain the activity of the perovskite which should contain overstoichiometric amounts of oxygen.[671] Likewise oxidation of $CH_2Cl_2$ with oxygen gas has been studied over $\delta$-alumina and $Al_2O_3-SiO_2$ in a wide range of different compositions.[672,673] Pure $SiO_2$ shows no activity.

Heavily polluted aqueous effluents cannot be treated realistically with oxidants other than oxygen. For these cases, the most common remediation procedure is "wet air oxidation", in which wastewater and oxygen or air are heated at high temperatures (150–400 °C) and pressures (20 MPa). Catalytic wet air oxidation can be an interesting alternative to classical wet air oxidation. The presence of a catalyst should make it possible to conduct more efficiently the degradation under not so extreme conditions of temperature and pressure. Low molecular weight carboxylic acids, which are the intermediary products formed in the course of some advanced oxidation techniques, are good model compounds to test the efficiency improvement of catalytic wet air oxidation. These simple carboxylic acids are among the most recalcitrant organic compounds to undergo further oxidative mineralization. Using transition metal ion-exchanged Y zeolites as catalysts and hydrogen peroxide as oxidizing reagent, it has been possible to effect the oxidation of acetic acid in aqueous solutions below the water boiling point.[674,675] A particularly effective catalyst for this catalytic, a wet air oxidation process was $Cu^{2+}$-exchanged Y zeolite in where the $Cu^{2+}$ was complexed with oxalic acid.[674,675] On the other hand, wastewaters containing both organic material and heavy metal ions, such as those from the photographic industry, can be treated with a combination of chemical oxidation and electrolysis.[676]

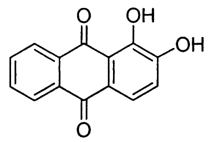
Some alkyl- or aryl-phosphonates are used as insecticides, and they may be present in surface waters in certain areas and periods. The decomposition can be carried out using air as oxidant at temperatures between 200 and 400 °C. Dimethyl methylphosphonate can be oxidatively decomposed using amorphous manganese oxide or alumina-supported manganese oxide as catalysts.[677] FTIR analysis suggests that dimethyl methylphosphonate strongly binds to the Mn Lewis acid sites on the manganese oxide surface through phosphoryl oxygens.[677]



$$CH_3-\underset{OCH_3}{\overset{\overset{O}{\|}}{P}}-OCH_3$$

Dimethyl methylphosphonate

Studies on the mechanisms of the oxidative degradation of organic compounds are scarce due to the complexity of the problem and the need to apply fast spectroscopic techniques. A pulse radiolysis study on the one electron oxidation of 1,2-dihydroxy-9,10-anthraquinone and its Cu(II), Ni(II), and Fe(III) complexes by hydroxyl radicals has provided evidence that in this case there are two reaction pathways involving the intermediacy of semiquinone radical cation or the OH-adduct, respectively.[678] The former path undergoes disproportionation, while the transition metal coordinated OH adduct leads to trihydroxyanthraquinone.



1,2-dihydroxy-9,10-anthraquinone

Photocatalytic oxidative degradation uses a semiconductor oxide such as $TiO_2$ or ZnO in combination or not with an organic dye that upon light absorption in aqueous medium generates hydroxyl radicals ($OH^{\bullet}$) and other reactive oxygen species (superoxide, singlet oxygen, etc.) that attack the organic material present in water and initiates its oxidative degradation.[679,680] Despite the general applicability of photocatalytic techniques, the two major limitations are the high energy costs associated to the irradiation, the need for more efficient photocatalysts and the requirement of transparency of the effluents.

The mechanism of acetonitrile photooxidation on $TiO_2$ has been investigated using IR spectroscopic.[681] At temperatures higher than −73 °C, the adsorption of $CH_3CN$ on both isolated Ti–OH groups and $Ti^{4+}$ Lewis acid sites was observed. Under UV irradiation ($h\nu$ 350 nm), $CH_3CN$ is oxidized in the presence of $O_2$ to form $CO_2$, $H_2O$, surface carbonate, and an intermediate isocyanate species. Photooxidation of the $CH_3$ moiety of acetonitrile occurs more easily than that of the $C\equiv N$.[681]

The effect of doping with transition metals on the photocatalytic activity of $TiO_2$ has been studied mechanistically by means of femtosecond pump–probe diffuse reflectance spectroscopy and also from preparative studies.[682] It was found that the second-order recombination rate constant of photogenerated electron and holes markedly increases with loading of the transition metal, even at low doping level (0.3%), and this correlates with the decrease in the rate of formation of the main products ($H_2$, $CO_2$, etc.) of the photocatalytic degradation.[682]

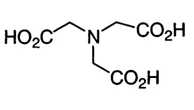
The photocatalytic activity of $TiO_2$ toward the decomposition of 1,4-dichlorobenzene in aqueous solution can be largely improved by loading with $WO_3$.[683] It was found that $WO_3$ covers the surface of $TiO_2$ with a monolayer. The resulting $WO_3/TiO_2$ disperse better in the aqueous solution than the pure $TiO_2$. For the gas-phase photooxidation of benzene and 2-propanol $WO_3/TiO_2$ shows 3.6–5.9 times the photocatalytic activity of pure $TiO_2$.[683]

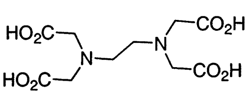
In situ FT-IR studies during the gas-phase photocatalytic oxidation of ethanol over $TiO_2$ have revealed that the photoactivity correlates with the surface acidity and the concentrations of $Ti^{3+}$ and carbonate surface concentration.[59]

Further improvements are still needed in the field of photocatalysis in terms of more efficient lamps, better match between lamp emission and photocatalyst absorption and higher quantum yields of $OH^{\bullet}$ generation.

Aerated aqueous solutions of $Fe_2(SO_4)_3$ have been reported to effect desulfuration of mineral raw materials, particularly coal, by oxidizing the sulfur to sulfate. A catalytic process to eliminate low-valent sulfur compounds present in water by adding hydrogen peroxide and a transition metal supported on alumina or silica has been patented.[684] Polysulfide can also be obtained by oxidation using oxygen containing gases in the presence of transition metals.[685,686]

A method and an apparatus to perform the biogas purification based on the aqueous oxidation of $H_2S$ to S at acidic pH has been devised.[687] The system uses $Fe^{3+}$ chelates of nitrilotriacetic and ethylendiaminotetracetic assisted by minor amounts of Cu or Ni salts and operates by reoxidizing the Fe after biogas treatment and recycling of the Fe-containing solution. Analogously, $H_2S$ and $SO_2$ can be removed from a gas stream by oxidation using a transition metal complex solution in water an a flotation cell.[688,689]


nitrilotriacetic acid

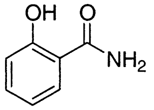

ethylendiaminotetraacetic acid

Homo- and copolymers derived of acrylamide can gelate aqueous solutions. It has been reported an interesting system in which one of such poly acrylamide hydrogels containing Fe, Ni, or Co salts is able to act as catalyst for the oxidation of $Na_2S$ with $O_2$ in aqueous solutions at 40 °C.[690]

In aqueous solution, the activity of a series of transition metal oxides supported on carbon has been determined for the catalytic oxidation of sulfide to elemental sulfur.[691] It was found these carbon-supported transition metal oxides have comparable activities to that of Co-phthalocyanines.[691]

The acid rain is caused by the burning of fuels with high S content. To avoid this serious environmental problem, legislations have been implemented to limit the maximum S content in fuels. A strategy to decrease the sulfur content in fuels is to oxidize the sulfur compounds transforming them in less volatile sulfoxides or sulfones that can be more easily separated from the fuel.

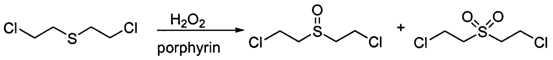
A procedure for sweetening the hydrocarbon feedstock by removing sulfur has been patented in which the catalyst is prepared by impregnation on active carbon or other solid support of an alcoholic solution of the catalyst that is a chelate of bis-salicylamide.[692] In a related process for purifying liquid organosulfur-containing hydrocarbons, an aqueous sulfuric acid solution containing transition metal is submitted to electrolysis to oxidize the metal ions to their highest oxidation state and, subsequently, the electrolyzed aqueous solution emulsified with the feedstock. This treatment removes organosulfur compounds from the hydrocarbon by converting them into a gas, or water soluble or resinous products.[693] The acid aqueous solution is separated and recycled via electrolysis.[693]


salicylamide

Molybdenum oxide supported on alumina ($MoO_3/Al_2O_3$ 12.5 wt %) has been nitrided by temperature programmed reaction with ammonia at various temperatures and their activity toward hydrodesulfuration of dibenzothiophene studied.[694] It was concluded that metallic $Mo^0$ and $Mo^{2+}$ are the most active species for the hydrodesulfuration.[694]

After international treaties to destroy chemical warfare stockpiles, there has been an interest in determining a suitable procedure to degrade mustard gas, one of the most widespread warfare chemicals.[695] Bleach is a suitable decontamination procedure for treating contaminated people or material,[696] but the proposed procedure for large scale destruction of contaminated material is incineration. This poses problems from the point of view of the environment. It has been reported that mustard gas can be transformed into the nontoxic corresponding sulfide and sulfone in aqueous media by hydrogen peroxide using metal *meso*-tetraarylporphyrin and imidazole or ammonium acetate as cocatalyst (Scheme 50).[697]

**Scheme 50**



The activity of metalloporphyrin depends markedly on the nature of the metal ($Fe^{3+}$ more efficient than $Mn^{3+}$). With the Fe metal complex, the oxygen transfer is fairly good (up to 95%) and the substrate/catalyst concentration ratio can be high (420).[697]

The kinetics of the aerobic oxidation of $SO_2$ in water at different pHs in the presence of transition metal ions has been studied.[698] Highly active clay composite for the removal of $SO_x$ from flue gas streams was obtained by precipitating $CaCO_3$ or $Ca(OH)_2$ onto the clay from an aqueous clay slurry and incorporating a transition metal oxide as finely divided metal oxide powder, metal salt or as clay-intercalated metal cation.[699] The clay acts as a dispersing agent for the base and the transition metal decreasing particle agglomeration and increasing the $SO_x$ uptake.

## D. Domestic and Technical Applications of Catalytic Oxidations

Besides the production of chemicals, Lewis acid catalyzed oxidations have also other curious applications that have impact in our daily life. In this section, we will provide some examples to give a flavor of the vast potential of catalytic oxidations.

A domestic application that takes advantage of the ability of catalytic oxidations by transition metal ions to effect the degradation of organic compounds is self-cleaning coatings for ovens. Besides water binders, hardening agents, and surfactants, the coating contains transition metal oxides deposited on activated alumina.[700,701]

The ability of transition metal ions in intermediate oxidation states to react with oxygen has been used in the formulation of adsorbent compositions to remove simultaneously oxygen and water from gas mixtures. A solution of a salt of Cr, Mn, V, or Mo in their higher oxidation states is adsorbed onto $SiO_2$ gel, alumina, or pumice stone and then reduced with $H_2$, CO, or coal gas.[702] On the other hand, a kit to determine quantitatively the oxygen content for aquarium application has been devised based on the presence of an oxidizable transition metal and a redox indicator capable of a color change upon oxidation of the metal salt. The resulting color is visually compared with a graduated scale.[703]

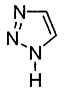
The combination of a bivalent transition metal or a transition metal complex of Mn. Co, Cu, Fe, and Ru with a peroxy compound or sodium perborate has been patented as a bleach-enchancer agent for cloth or dish washing, cleaning and disinfection.[704−706] After treating aqueous solutions of alkyl polyglycoside surfactants with a peroxide-decomposing transition metal, addition of hydrogen peroxide can be used to bleach the color of these solutions.[707]

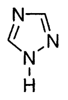
Catalytic oxidation at temperatures below 100 °C and atmospheric pressure is the key step in a procedure for the treatment of malodorous gas. First, the gases are contacted with a scrubbing water to adsorb the malodorous components. The aqueous medium contains an alkali, alkaline-earth, or transition metal ion as catalyst and optionally a solid oxide as support.[708]

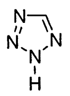
Another use of transition metal-catalyzed oxidation is in shrink proofing fibers to effect the decomposition of the keratin layer on natural fibers using $H_2O_2$ as oxidizing reagent.[709]

Transition metal ions can also catalyze the explosive decomposition of inorganic oxidizer salt. Thus, the major component of a detonator has been manufactured by adding significant amounts (0.2−10%) of transition metals (Cr, Co, Cu, and Mn) as a mixed alkali metal phosphate or as a complex to hot aqueous solutions of $NH_4NO_3$ and filtrating the precipate upon cooling the solution to ambient temperature.[710]

Triazole and tetrazole in combination with an oxidizer, a transition metal oxide, and chlorates or perchlorates are the chemical components of the gas generating charges for airbag inflation.[711] Triazole or tetrazole have replaced more toxic and unstable azide-based compounds as propellant in airbag inflation devices. A transition metal oxide such as CuO is required to catalyze the explosive autoignition decomposition of the nitrogenated pentacyclic heterocycle at around 170 °C.[712,713]


1,2,3-triazole


1,2,4-triazole


tetrazole

## V. Conclusions

In this review, we have shown the evolution from homogeneous Lewis acids as catalysts to solid “oxidation catalysts”. The simplest strategy in which the Lewis acid is deposited on a solid surface has evolved to more elaborate ones in which the Lewis site forms part of the solid framework. Titanium silicalite is the most emblematic example of this type of solid oxidation catalysts.

Soon, it can be foreseen that the lead initiated by TS-1 will continue. New solids in which framework transition metals exhibit Lewis acidity will be synthesized and tested as oxidation catalysts. The acid strength and oxidation activity of the Lewis site will be modulated and adjusted to the reaction requirements by careful control of the chemical composition of the coordination sphere. The substrate and reagent concentration around the site will be controlled by modifying the hydrophilicity/hydrophobicity of the solid.

The centers will be designed inspired not only on homogeneous Lewis acids, but also learning from the active centers of enzymes and biomolecules. Bioinspiration and molecular modeling will emerge as powerful strategies in catalyst design. These tools will be accompanied by new synthetic procedures in which the solids will be manipulated at the atomic level to assemble clusters that could act as active centers. For multifunctional catalysts, the sites will be located at the required distance and with the necessary strength. The combination of all these new approaches will necessarily result in more efficient, active, and environmentally friendly solid catalysts, particularly for the selective oxidation of alkanes or using oxygen as an oxidant.

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## VII. References

(1) Muzart, J. *Chem. Rev.* **1992**, *92*, 113.
(2) Sheldon, R. A. In *Catalytic Oxidations in the Manufacture of Fine Chemicals, New Developments in Selective Oxidation*; Centi, G., Trifiro, F., Eds.; Elsevier Science Publishers B. V.: Amsterdam, 1990.
(3) Sheldon, R. A. In *Redox Molecular Sieves as Heterogeneous Catalysts for Liquid-Phase Oxidations, 3rd World Congress on Oxidation Catalysis*; Grasselli, R. K., Gaffney, A. M., Oyama, S. T., Lyons, J. E., Eds.; Elsevier Science B. V.: New York, 1997; Vol. 110, pp 151−175.
(4) Hölderich, W. F. *New Frontiers in Catalysis*; Elsevier Science: Amsterdam, The Netherlands, 1992; pp 145−150.
(5) Hammerich, O.; Parker, V. D. In *Kinetics and Mechanisms of Reactions of Organic Cation Radicals in Solution, Adv. Phys. Org. Chem.*; Academic Press: London, 1984; Vol. 20, pp 55−189.
(6) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243−250.
(7) Bard, A. J.; Ledwith, A.; Shine, H. J. In *Formation, Properties and Reactions of Cation Radicals in Solution, Adv. Phys. Org. Chem.*; Academic Press: London, 1976; Vol. 12, pp 155−278.
(8) Aeiyach, S.; Soubiran, P.; Lacaze, P. C.; Froyer, G.; Pelous, Y. *Synth. Met.* **1995**, *68*, 213−19.

(9) Bodem, N.; Bushby, R. J.; Clements, J. *J. Chem. Phys.* **1993**, *98*, 5920−31.
(10) Bodem, N.; Bushby, R. J.; Clements, J. *J. Mater. Sci.* **1994**, *5*, 83−8.
(11) Dabestani, R.; Nelson, M.; Sigman, M. E. *Photochem. Photobiol.* **1996**, *64*, 80−86.
(12) Eberson, L.; Persson, O. *Acta Chem. Scand.* **1996**, *50*, 395−398.
(13) Estermann, G. H.; Crockett, R.; Roduner, E. *Stud. Surf. Sci. Catal.* **1995**, *98*, 73−4.
(14) Crockett, R.; Roduner, E. *J. Chem. Soc., Perkin Trans. 2* **1994**, 347−50.
(15) Orabi, A. S.; Ayad, M. I.; Ramadan, A. E.-M. M. *Transition Met. Chem.* **1998**, *23*, 391−396.
(16) Oyaizu, K.; Iwasaki, N.; Yamamoto, K.; Nishide, H.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1456−61.
(17) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600−610.
(18) Bein, T. *Stud. Surf. Sci. Catal.* **1996**, *102*, 295−322.
(19) Benvenuti, F.; Galletti, A. M. R.; Carlini, C.; Sbrana, G.; Nannini, A.; Bruschi, P. *Polymer* **1997**, *38*, 4973−4982.
(20) Kossmehl, G.; Bischoff, R.; Betz, G. *Polym. J.* **1994**, *26*, 179−85.
(21) Sato, M.; Amano, K.; Ishikwa, H., Japan Patent JP07118371, 1995.
(22) Rapi, S.; Bocchi, V.; Gardini, G. *Synth. Met.* **1988**, *24*, 217−221.
(23) Takakubo, M.; Osawa, T., Japan Patent JP85−219113, 1987.
(24) Kaneko, B.; Ariizumi, A.; Akira, H.; Yanagisawa, A.; Kamyama, M., Japan Patent, JP07286035, 1995.
(25) Yamamoto, R., Jpn. Kokai Tokkyo Koho, JP93−40492, 1994.
(26) Tran, V. H.; Guyot, A.; Nguyen, T. P.; Molinie, P. *Polym. Degrad. Stab.* **1995**, *49*, 331−7.
(27) Védrine, J. C. *Catal. Oxid.* **1995**, 53−78.
(28) Védrine, J. C.; Coudurier, G.; Millet, J.-M. M. *Catal. Today* **1997**, *33*, 3−13.
(29) Doornkamp, C.; Ponec, V. *J. Mol. Catal. A* **2000**, *162*, 19−32.
(30) Schlogl, R.; Knop-Gericke, A.; Havecker, M.; Wild, U.; Frickel, D.; Ressler, T.; Jentoft, R. E.; Wienold, J.; Mestl, G.; Blume, A.; Timpe, O.; Uchida, Y. *Top. Catal.* **2001**, *15*, 219−228.
(31) Védrine, J. C.; Millet, J. M. M.; Volta, J.-C. *Catal. Today* **1996**, *32*, 115−123.
(32) Védrine, J. C. *Stud. Surf. Sci. Catal.* **1997**, *110*, 61−76.
(33) Védrine, J. C.; Coudurier, G.; Ouqour, A.; Pries de Oliveira, P. G.; Volta, J.-C. *Catal. Today* **1996**, *28*, 3−15.
(34) Védrine, J. C.; Millet, J. M. M.; Volta, J.-C. *Catal. Today* **1996**, *32*, 115−123.
(35) Watanabe, H.; Koyasu, Y. *Appl. Catal. A* **2000**, *479*, 194−195.
(36) Seiyama, T.; Egashira, M.; Sakamoto, T.; Aso, I. *J. Catal.* **1972**, *24*, 76.
(37) Dadyburjor, D. B.; Jewur, S. S.; Ruckenstein, E. *Catal. Rev. Sci. Eng.* **1979**, *19*, 76.
(38) Belokpytov, Y.; Kholyavalenko, K. M.; Ya, M. *Rubanik Kinet. Katal.* **1973**, *14*, 1280.
(39) Gai, P. L.; Kourtakis, K. *Science* **1995**, *267*, 661−3.
(40) Bordes, E. *C. R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 725−733.
(41) Zazhigalov, V. A.; Nieto, J. M. L.; Solsona, B.; Komashko, G. A.; Bacherikova, I. V.; Stoch, J. *Theor. Exp. Chem.* **2000**, *35*, 275−279.
(42) Gadgil, M. M.; Kulshreshtha, S. K. *J. Solid State Chem.* **1994**, *111*, 357−64.
(43) Bentrup, U.; Bruckner, A.; Martin, A.; Lucke, B. *J. Mol. Catal. A* **2000**, *162*, 383−391.
(44) Savary, L.; Saussey, J.; Costentin, G.; Bettahar, M. M.; Gubelmann-Bonneau, M.; Lavalley, J. C. *Catal. Today* **1996**, *32*, 57−61.
(45) Wachs, I. E.; Jehng, J.-M.; Deo, G.; Weckhuysen, B. M.; Guliants, V. V.; Benziger, J. B. *Catal. Today* **1996**, *32*, 47−55.
(46) Chen, B.; Munson, E. J. *J. Am. Chem. Soc.* **2002**, *124*, 1638−1652.
(47) Trifiro, F. *Chim. Ind.* **1994**, *76*, 524−5.
(48) Koyano, G.; Saito, T.; Misono, M. *J. Mol. Catal. A* **2000**, *155*, 31−41.
(49) Batis, N. H.; Ghhorbel, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1997**, *94*, 77−92.
(50) Guliants, V. V.; Benziger, J. B.; Sundaresan, S.; Wachs, I. E.; Hirt, A. M. *Catal. Lett.* **1999**, *62*, 87−91.
(51) Carrara, C.; Irusta, S.; Lonbardo, E.; Cornalia, L. *Appl. Catal. A* **2001**, *217*, 275−286.
(52) Mastuura, I.; Ishimura, T.; Hayakawa, S.; Kimura, N. *Catal. Today* **1996**, *28*, 133−138.
(53) Cornaglia, L. M.; Lombardo, E. A.; Anderson, J. A.; Garcia Fierro, J. L. *Appl. Catal. A* **1993**, *100*, 37−50.
(54) Centi, G.; Perathoner, S. *J. Catal.* **1993**, *142*, 84−96.
(55) Centi, G. *Appl. Catal. A.* **1996**, *147*, 267.
(56) Deo, G.; Wachs, I. E.; Haber, J. *Crit. Rev. Surf. Chem.* **1994**, *4*, 141.
(57) Bond, G. C.; Tahir, S. F. *Appl. Catal* **1991**, *71*, 1.
(58) Blasco, T.; Lopez Nieto, J. M. *Appl. Catal. A.* **1997**, *157*, 117.
(59) Kozlov, D. V.; Paukshtis, E. A.; Savinov, E. N. *Appl. Catal. B* **2000**, *24*, L7-L12.
(60) Ledo, B.; Rives, V.; Sanchez-Escribano, V.; Busca, G. *Catal. Lett.* **1993**, *18*, 329−35.
(61) Blasco, T.; Lopez Nieto, J. M.; Dejoz, A.; Vazquez, M. I. *J. Catal.* **1995**, *157*, 271−82.
(62) Garcia, H.; López-Nieto, J. M.; Palomares, E.; Solsona, B. *Catal. Lett.* **2000**, *69*, 217−221.
(63) Baltes, M.; Kytoekivi, A.; Weckhuysen, B. M.; Schoonheydt, R. A.; Van Der Voort, P.; Vansant, E. F. *J. Phys. Chem. B* **2001**, *105*, 6211−6220.
(64) Chen, K.; Bell, A. T.; Iglesia, E. *J. Phys. Chem. B* **2000**, *104*, 1292−1299.
(65) Concepción, P.; Kuba, S.; Knozinger, H.; Solsona, B.; López-Nieto, J. M. *Stud. Surf. Sci. Catal.* **2000**, *130A*, 767−772.
(66) Pantazidis, A.; Auroux, A.; Herrmann, J. M.; Mirodatos, C. *Catal. Today* **1996**, *32*, 81−88.
(67) Wachs, I. E.; Jehng, J.-M.; Deo, G.; Weckhuysen, B. M.; Guliants, V. V.; Benziger, J. B.; Sundaresan, S. *J. Catal.* **1997**, *170*, 75−88.
(68) Sun, Q.; Jehng, J.-M.; Hu, H.; Herman, R. G.; Wachs, I. E.; Klier, K. *J. Catal.* **1997**, *165*, 91−101.
(69) Wachs, I. E.; Briand, L. E.; Jehng, J. M.; Burcham, L.; Gao, X. *Catal. Today* **2000**, *57*, 323−330.
(70) Ramis, G.; Busca, G.; Lorenzelli, V. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1293−9.
(71) Baerns, M.; Buyevskaya, O. V.; Kubik, M.; Maiti, G.; Ovsitser, O.; Seel, O. Book of Abstracts, 210th ACS National Meeting, Chicago, IL, August 20−24, 1995, COLL-053.
(72) Miyata, H.; Ohno, T.; Hatayama, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3505−10.
(73) Martin, A.; Lucke, B. *Chem. Ind.* **2001**, *82*, 337−348.
(74) Nobbenhuis, M. G.; Hug, P.; Mallat, T.; Baiker, A. *Appl. Catal. A* **1994**, *108*, 241−60.
(75) Hölderich, W. F. *Appl. Catal. A* **2000**, *194−195*, 487−496.
(76) Zanthoff, H. W.; Grunert, W.; Buchholz, S.; Heber, M.; Stievano, L.; Wagner, F. E.; Wolf, G. U. *J. Mol. Catal. A* **2000**, *162*, 435−454.
(77) Centi, G.; Marchi, F.; Perathoner, S. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 5151−5159.
(78) Kooli, F.; Martin, C.; Rives, V. *Langmuir* **1997**, *13*, 2303−2306.
(79) Ghenciu, A.; Farcasiu, D. *J. Chem. Soc., Chem. Commun.* **1996**, 169−170.
(80) Farcasiu, D.; Ghenciu, A.; Li, J. Q. *J. Catal.* **1996**, *158*, 116−127.
(81) Riemer, T.; Knoezinger, H. *J. Phys. Chem.* **1996**, *100*, 6739−42.
(82) Sohn, J. R.; Ryu, S. G. *Langmuir* **1993**, *9*, 126−31.
(83) Shitova, N. B.; Drozdov, V. A.; Kolosov, P. E.; Smolikov, M. D. *Kinet. Catal.* **2000**, *41*, 720−728.
(84) Pestryakov, A. N.; Lunin, V. V.; Bogdanchikova, N. E.; Petranovskii, V. P. Abstracts of Papers, 222nd ACS National Meeting, Chicago, 2001; p COLL-067.
(85) Burcham, L. J.; Briand, L. E.; Wachs, I. E. *Langmuir* **2001**, *17*, 6164−6174.
(86) Burcham, L. J.; Briand, L. E.; Wachs, I. E. *Langmuir* **2001**, *17*, 6175−6184.
(87) Rajagopal, S.; Marzari, J. A.; Miranda, R. *J. Catal.* **1995**, *151*, 192−203.
(88) Markaryan, G. L.; Lunina, E. V. *Kinet. Catal.* **1996**, *37*, 133−9.
(89) Lercher, J. A.; Bitter, J. H.; Hally, W.; Niessen, W.; Seshan, K. *Stud. Surf. Sci. Catal.* **1996**, *101*, 463−472.
(90) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603−605.
(91) Dai, H.; Hafner, n. J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147−150.
(92) Liu, S.; Xu, L.; Xie, S.; Wang, Q.; Xiong, G. *Appl. Catal. A* **2001**, *211*, 145−152.
(93) Hatano, M.; Otsuka, K. *Inorg. Chim. Acta* **1988**, *146*, 243−247.
(94) Ivanova, A. S.; Paukshtis, E. A.; Sobyanin, V. A.; Galvita, V. V. *React. Kinet. Catal. Lett.* **1998**, *64*, 337−342.
(95) Weiss, W.; Schlogl, R. *Top. Catal.* **2000**, *13*, 75−90.
(96) Frusteri, F.; Arena, F.; Martra, G.; Coluccia, S.; Mezzapica, A.; Parmaliana, A. *Catal. Today* **2001**, *64*, 97−102.
(97) Wang, C.-T.; Willey, R. J. *J. Catal.* **2001**, *202*, 211−219.
(98) del Arco, M.; Martin, C.; Rives, V.; Sanchez-Escribano, V.; Ramis, G.; Busca, G.; Lorenzelli, V.; Malet, P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1071−8.
(99) Centeno, M. A.; Capitan, M. J.; Bosch, P.; Malet, P.; Benitez, J. J.; Carrizosa, I.; Odriozola, J. A. *J. Mater. Chem.* **1995**, *5*, 175−81.
(100) Tsodikov, M. V.; Kugel, V. Y.; Slivinskii, E. V.; Bondarenko, G. N.; Maksimov, Y. V.; Alvarez, M. A.; Hidalgo, M. C.; Navio, J. A. *Appl. Catal. A* **2000**, *193*, 237−242.
(101) Rogovin, M.; Neumann, R. *J. Mol. Catal. A* **1999**, *138*, 315−318.
(102) Baardman, F.; Jubb, J., PCT Int. Appl., WO 9731969, 1997.
(103) Bulanin, K. M.; Lavalley, J. C.; Tsyganenko, A. A. *Colloids Surf., A* **1995**, *101*, 153−8.
(104) Davydov, A. A. *Kinet. Katal.* **1993**, *34*, 699−702.
(105) Coulson, D. R.; Wijnen, P. W. J. G.; Lerou, J. J.; Manzer, L. E. *J. Catal.* **1993**, *140*, 103−20.

(106) Bartosova, M.; Cerveri, L.; Vicnerlara, B. *Chem. Listy* **2001**, *95*, 278−282.
(107) Sheldon, R. A. *Curr. Top. Flavours Fragrances* **1999**, 59−78.
(108) Cornélis, A.; Laszlo, P. *Synthesis* **1987**, 909.
(109) Delaude, L.; Laszlo, P.; Smith, K. *Acc. Chem. Res.* **1993**, *26*, 607−613.
(110) Laszlo, P.; Levart, M. *Tetrahedron Lett.* **1993**, *34*, 1127−1130.
(111) Jamis, J.; Drljaca, A.; Spiccia, L.; Smith, T. D. *Chem. Mater.* **1995**, *7*, 2086−9.
(112) Lenarda, M.; Ganzerla, R.; Storaro, L.; Enzo, S.; Zanoni, R. *J. Mol. Catal.* **1994**, *92*, 201−15.
(113) Palombi, L.; Bonadies, F.; Scettri, A. *J. Mol. Catal. A* **1999**, *140*, 47−53.
(114) Notari, B. *Adv. Catal.* **1996**, *41*, 253.
(115) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202−6208.
(116) Ballisteri, F. P.; Tomaselli, G. A.; Toscano, R. M.; Conte, V.; Di Furia, F. *J. Am. Chem. Soc.* **1991**, *113*, 6209−6212.
(117) Bonchio, M.; Calloni, S.; Di Furia, F.; Licini, G.; Modena, G.; Moro, S.; Nugent, W. A. *J. Am. Chem. Soc.* **1997**, *119*, 6935−6936.
(118) Kijenski, J.; Baiker, A. *Catal. Today* **1989**, *5*, 1.
(119) Germanin, J. E. *Intra-Science Chem. Rep.* **1972**, *6*, 101.
(120) Margolus, L. Y.; Firsowa, A. A. *Prob. Kinet. Catal.* **1975**, *16*, 98.
(121) Haber, J. Proc. Pol. 8th Int. Congr. Catal, Krakow, 1988; p 85.
(122) Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1974**, *35*, 1839.
(123) Arends, I. W. C. E.; Sheldon, R. A.; Wallau, M.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1144.
(124) Hamamoto, S.; Shimano, T., Jpn. Kokai Tokkyo Koho, JP 09249606, 1997.
(125) Lau, T.-C.; Wu, Z.-B.; Bai, Z.-L.; Mak, C.-K. *J. Chem. Soc., Dalton Trans.* **1995**, 695−6.
(126) Ho, C.-M.; Lau, T.-C. *New J. Chem.* **2000**, *24*, 587−590.
(127) Lau, T. C.; Mak, C. K. *J. Chem. Soc., Chem. Commun.* **1993**, 766−7.
(128) Sugimura, T.; Fujiwara, Y.; Tai, A. *Tetrahedron Lett.* **1997**, *38*, 6019−6022.
(129) Xie, N.; Binstead, R. A.; Block, E.; Chandler, W. D.; Lee, D. G.; Meyer, T. J.; Thiruvazhi, M. *J. Org. Chem.* **2000**, *65*, 1008−1015.
(130) Firouzabadi, H.; Mohammadpoor-Baltork, I. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2319−25.
(131) Tamami, B.; Zarchi, M. A. K. *Eur. Polym. J.* **1995**, *31*, 715−17.
(132) Wu, M.-h.; Yang, G.-c.; Chen, Z.-x. *Youji Huaxue* **2000**, *20*, 808−811.
(133) Li, Y.-M. *Hecheng Huaxue* **2000**, *8*, 371−374.
(134) Firouzabadi, H.; Sardarian, A.; Badparva, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 685−91.
(135) Firouzabadi, H.; Mohammadpoor-Baltork, I. *Synth. Commun.* **1994**, *24*, 1065−77.
(136) Li, Y.; Matsuda, M.; Thiemann, T.; Sawada, T.; Mataka, S.; Tashiro, M. *Synlett* **1996**, 461−464.
(137) Sartori, G.; Maggi, R.; Bigi, F.; Arienti, A.; Mori, G. *J. Chem. Res., Synop.* **1995**, 212.
(138) Figiel, P. J.; Sobczak, J. M. *Pol. J. Chem.* **2001**, *75*, 869−873.
(139) Lane, B. L.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 2933.
(140) Rothenberg, G.; Clark, J. H. *Green Chem.* **2000**, *2*, 248−251.
(141) Rotherberg, G.; Clark, J. *Org. Proc. Res. Dev.* **2000**, *4*, 270−274.
(142) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H., PCT Int. Appl., WO 9850333, 1998.
(143) Manov, V. *Biotekhnol. Khim.* **1989**, *1*, 18−20.
(144) Dakka, J.; Zoran, A.; Sasson, Y. P., Eur. Patent, EP88−401921, 1989.
(145) Arima, F., Patent, JP 07291896, 1995.
(146) Iida, S.; Hasebe, R.; Saito, N., JP10095746A2, 1998.
(147) Ito, I.; Yokota, K.; Sato, T., Patent, JP 06345685, 1994.
(148) Neubauer, G.; Schnabel, R.; Hartig, J.; Ritz, J., AL19880428, 1988.
(149) Tsou, C.; Lin, S.; Huang, T.; Shen, C., 1S99−239761, 2000.
(150) Elizarova, G.; Matvienko, L.; Kuzmin, A.; Saginova, E.; Parmon, V. *Mendeleev Commun.* **2001**, *1*, 15−17.
(151) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structures*; 3rd ed.; McGraw-Hill: New York, 1993.
(152) de Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. *Synthesis* **1994**, 1007−17.
(153) Okano, T.; Matsuoka, M.; Kinoshita, M.; Kiji, J. *Nippon Kagaku Kaishi* **1993**, 487−92.
(154) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5664−5665.
(155) Nait, A. *Tetrahedron Lett.* **2001**, *42*, 13−15.
(156) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189−6190.
(157) Herrmann, W. A.; Zoller, J. P.; Fischer, R. W. Book of Abstracts, 218th ACS National Meeting, New Orleans, Aug. 22−26, 1999, INOR-272.
(158) Fischer, R. W.; Herrmann, W. A.; Weskamp, T., PCT Int. Appl., WO 9847852, 1998.
(159) Fischer, R. W.; Haider, J.; Herrmann, W. A.; Kratzer, R., PCT Int. Appl., WO 9847837, 1998.
(160) Wang, W.-D.; Espenson, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 11335−11341.
(161) Gable, K. P.; AbuBaker, A. Book of Abstracts, 213th ACS National Meeting, San Francisco, April 13−17, 1997, ORGN-638.
(162) Thiel, W. R.; Eppinger, J. *Chem. Eur. J.* **1997**, *3*, 696−705.
(163) Thiel, W. R. *Chem. Ber.* **1996**, *129*, 575−580.
(164) Nair, V.; Mathew, J.; Prabhakaran, J. *Chem. Soc. Rev.* **1997**, *26*, 127−132.
(165) Baciocchi, E.; Ruzziconi, R. *NATO ASI Ser., Ser. C* **1989**, *260*, 155−85.
(166) Chapuzet, J.-M.; Beauchemin, S.; Daoust, B.; Lessard, J. *Tetrahedron* **1996**, *52*, 4175−80.
(167) Ganin, E.; Amer, I. *J. Mol. Catal. A* **1997**, *116*, 323−327.
(168) Martyn, L. J. P.; Pandiaraju, S.; Yudin, A. K. *J. Organomet. Chem.* **2000**, *603*, 98−104.
(169) Akamatsu, T.; Kobayashi, T.; Sasaki, Y.; Ito, S.; Nishida, Y. *Polyhedron* **1997**, *16*, 1497−1503.
(170) Nguyen, S. T.; Paddock, R. L. *J. Am. Chem. Soc.* **2001**, *123*, 11498.
(171) Iseki, Y.; Kudo, M.; Mori, A.; Inoue, S. *J. Org. Chem.* **1992**, *57*, 6329−31.
(172) Gurevich, M. A.; Gus'kov, A. K.; Makarov, M. G.; Suchkov, Y. P.; Petrovich, E. N.; Shvets, V. F. *Kinet. Catal.* **1995**, *36*, 788−91.
(173) Carroll, K. M., U.S. Patent 6380406, 2002.
(174) Kreher, U.; Schebesta, S.; Walther, D. *Z. Anorg. Allg. Chem.* **1998**, *624*, 602−612.
(175) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974−5976.
(176) Finn, M. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 113−126.
(177) Potvin, P. G.; Branchet, S. *J. Org. Chem.* **1992**, *57*, 629−6635.
(178) Woodard, S. S.; Finn, M. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 106−113.
(179) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063.
(180) Jacobsen, E. N.; Zhang, W.; Güller, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 3, 6703.
(181) Jacobsen, E. N.; Zhang, W. *J. Org. Chem.* **1991**, *56*, 2296−2298.
(182) Yamashita, Y.; Katsuki, T. *Synlett* **1995**, 829−30.
(183) Adam, W.; Hajra, S.; Herderich, M.; Saha-Moeller, C. R. *Org. Lett.* **2000**, *2*, 2773−2776.
(184) Jager, E.-G.; Knaudt, J.; Schuhmann, K.; Guba, A. *Peroxide Chem.* **2000**, 249−280.
(185) Turner, J. F. C.; Theopold, K. H. Book of Abstracts, 212th ACS National Meeting, Orlando, FL, August 25−29, 1996, INOR-009.
(186) Parton, R. F.; Uytterhoeven, L.; Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1991**, *59*, 395−403.
(187) Herron, N.; Stucky, G. D.; Tolman, C. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1521−1522.
(188) Dolphin, D. H.; Nakano, T.; Kirk, T. K.; Maione, T. E.; Farrell, R. L.; Wijesekera, T. P., WO 88-US1240 19880415, 1998.
(189) Sorokin, A.; Meunier, B. *J. Chem. Commun., Chem. Soc.* **1994**, 1799−1780.
(190) Goodwin, J.; Bailey, R.; Pennington, W.; Rasberry, R.; Green, T.; Shasho, S.; Yongsavanh, M.; Echevarria, V.; Tiedeken, J.; Brown, C.; Fromm, G.; Lyerly, S.; Watson, N.; Long, A.; De Nitto, N. *Inorg. Chem.* **2001**, *40*, 4217−4225.
(191) Nguyen, S. T.; Hupp, J. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4239.
(192) Merlau, M. L.; Mejía, M. P.; Nguyen, S. T.; Hupp, J. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4239.
(193) Merlau, M. L.; Grande, W. J.; Nguyen, S. T.; Hupp, J. T. *J. Mol. Catal. A* **2000**, *156*, 79−84.
(194) Merlau, M. L.; Grande, W. J.; Nguyen, S. T.; Hupp, J. T. Book of Abstracts, 217th ACS National Meeting, Anaheim, Calif., March 21−25, 1999, ORGN-453.
(195) Grande, W. J.; Merlau, M.; Nguyen, S. T.; Hupp, J. T. Book of Abstracts, 217th ACS National Meeting, Anaheim, Calif., March 21−25, 1999, CHED-157.
(196) Schumann, H. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 1494−504.
(197) Shao, P.; Gendron, R. A. L.; Berg, D. J. *Can. J. Chem.* **2000**, *78*, 255−264.
(198) Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2057−2059.
(199) Horvath, I. T. *Aqueous-Phase Organomet. Catal.* **1998**, 548−554.
(200) Horvath, I. T. Book of Abstracts, 216th ACS National Meeting, Boston, August 23−27, 1998, FLUO-019.
(201) Horvath, I. T. Book of Abstracts, 211th ACS National Meeting, New Orleans, LA, March 24−28, 1996, ANYL-168.
(202) Horvath, I. T.; Rabai, J. *Science* **1994**, *266*, 72−5.
(203) Montanari, F.; Pozzi, G.; Quici, S. *Chim. Ind.* **1998**, *80*, 469−476.
(204) Cavazzini, M.; Montanari, F.; Pozzi, G.; Quici, S. *J. Fluorine Chem.* **1999**, *94*, 183−193.
(205) Sheldon, R. *Chem. Commun.* **2001**, 2399−2407.
(206) Ravikumar, K. S.; Kesavan, V.; Bonnet-Delpon, D.; Begue, J.-P. *Abstr. Pap. Am. Chem. Soc.* **2000**, *220th*, IEC-003.

(207) Suresh, A. K.; Sharma, M. M.; Sridhar, T. *Ind. Eng. Chem. Res.* **2000**, *39*, 3958−3997.
(208) Betzemeier, B.; Knochel, P. *Peroxide Chem.* **2000**, 454−468.
(209) Betzemeier, B.; Lhermitte, F.; Knochel, P. *Synlett* **1999**, 489−491.
(210) Betzemeier, B.; Lhermitte, F.; Knochel, P. *Tetrahedron Lett.* **1998**, *39*, 6667−6670.
(211) Pozzi, G. Book of Abstracts, 216th ACS National Meeting, Boston, August 23−27, 1998, FLUO-023.
(212) Nishimura, T.; Maeda, Y.; Kakiuchi, N.; Uemura, S. *J. Chem. Soc., Perkin 1* **2000**, 4301−4305.
(213) Betzemeier, B.; Cavazzini, M.; Quici, S.; Knochel, P. *Tetrahedron Lett.* **2000**, *41*, 4343−4346.
(214) Colonna, S.; Gaggero, N.; Montanari, F.; Pozzi, G.; Quici, S. *Eur. J. Org. Chem.* **2001**, 181−186.
(215) Izumi, Y.; Urabe, K. *Stud. Surf. Sci. Catal.* **1994**, *90*, 1−8.
(216) Izumi, Y. *Res. Chem. Interm.* **1998**, *24*, 461−471.
(217) Izumi, Y. In *Silica-Occluded Heteropolyacids, Fine Chemicals through Heterogeneous Catalysis*; Sheldon, R. A., van Bekkum, H., Eds.; Wiley-VCH: Weinheim, 2001; pp 100−105.
(218) Misono, M.; Ono, I.; Koyano, G.; Aoshima, A. *Pure Appl. Chem.* **2000**, *72*, 1305−1311.
(219) Jansen, R. J. J.; van Veldhuizen, H. M.; Schwegler, M. A.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 115−35.
(220) Moffat, J. B. *Chem. Eng. Commun.* **1989**, *83*, 9−29.
(221) Aranzabe, A.; Roman, P.; Aguayo, A. T.; Martin, C.; Rives, V. *Spectrosc. Lett.* **1997**, *30*, 963−974.
(222) Faraj, M.; Lin, C.; Hill, C. *New J. Chem.* **1988**, *12*, 745−749.
(223) Chen, Q.; Hill, C. 214th ACS National Meeting, Las Vegas, 1997; p INOR-132.
(224) Cavani, F.; Etienne, E.; Favaro, M.; Galli, A.; Trifiro, F.; Hecquet, G. *Catal. Lett.* **1995**, *32*, 215−26.
(225) Li, W.; Oshihara, K.; Ueda, W. *Appl. Catal. A* **1999**, *182*, 357−363.
(226) Li, H.; Shu, H.; Ye, X.; Wu, Y. *Huaxue Jinzhan* **2001**, *13*, 461−471.
(227) Neuman, R.; Cohen, M. *Angew. Chem.* **1997**, *109*, 1810.
(228) Goetz, P.; Wieland, S.; Panster, P.; Goor, G.; Siegmeier, R., U.S. Patent 5286885, 1994.
(229) Villa, A. L.; Sels, P. B. F.; De Vos, D. E.; Jacobs, P. A. *J. Org. Chem.* **1999**, *64*, 7267.
(230) Asahi, Y.; Iida, Y.; Sasaki, Y., Japan Patent JP09169694, 1997.
(231) Toujima, M.; Iida, Y.; Nakashima, Y.; Sasaki, Y., Japan Patent, JP97−156435, 1999.
(232) Anunziata, O. A.; Eimer, G. A.; Pierella, L. B. *Catal. Lett.* **2001**, *75*, 93−97.
(233) Weinstock, I.; Atalla, R.; Hill, C., WO 9526438, 1995.
(234) Atalla, R.; Weinstock, I.; Hill, C.; Reiner, R., US94−224449, 1996.
(235) Weinstock, I. A.; Barbuzzi, E. M. G.; Wemple, M. W.; Cowan, J. J.; Reiner, R. S.; Sonnen, D. M.; Heintzt, R. A.; Bond, J. S.; Hill, C. L. *Nature* **2001**, *414*, 191−195.
(236) Weinstock, I.; Hammel, K.; Moen, M.; Landucci, L.; Ralph, S.; Sullivan, C.; Riner, R. *Holzforschung* **1998**, *52*, 311−318.
(237) Gao, F.; Zhong, S. *Cuihua Xuebao* **2000**, *21*, 574−578.
(238) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: London, 1978.
(239) *Guidelines for Mastering the Properties of Molecular Sieves. Relationship Between the Physicochemical Properties of Zeolitic Systems and their Low Dimensionality*; Barthomeuf, D.; Derouane, E. G.; Hölderich, W., Eds.; Plenum Press: New York, 1990.
(240) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; John Wiley and Sons: New York, 1974.
(241) *Zeolite Microporous Solids: Synthesis, Structure and Reactivity*; Derouane, E. G.; Lemos, F.; Naccache, C.; Ramoa Ribeiro, F., Eds.; Kluwer Academic: Dordrecht, 1992; Vol. 352.
(242) *Introduction to Zeolite Science and Practice*; van Bekkum, H.; Flanigen, E. M.; Jansen, J. C., Eds.; Elsevier: Amsterdam, 1991.
(243) Townsend, R. P. In *Ion Exchange in Zeolites, Introduction to Zeolite Science and Practice*; van Bekkum, H., Flanigen, E. M., Jansen, J. C., Eds.; Elsevier: Amsterdam, 1991; Vol. 58, pp 359−390.
(244) McDaniel, C. V.; Maher, P. K. In Zeolite Chemistry and Catalysis, *ACS Monograph*; Rabo, J. A., Ed.; American Chemical Society: Washington, DC, 1976; Vol. 171, p 285.
(245) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Butterworth: London, 1992.
(246) Meier, W. M.; Olson, D. H.; Baerlocher, C. *Zeolites* **1996**, *17*, 1−229.
(247) Corma, A. *Chem. Rev.* **1995**, *95*, 559−614.
(248) Ward, J. W.; Hansford, R. C. *J. Catal.* **1964**, *13*, 364.
(249) Rabo, J. A.; Gajda, G. J. *Catal. Rev. Sci. Eng.* **1989**, *31*, 385−430.
(250) Corma, A.; García, H.; Primo, J. *J. Chem. Res. (S)* **1988**, 40−41.
(251) Mirodatos, C.; Barthomeuf, D. *J. Chem. Commun., Chem. Soc.* **1981**, 39.
(252) Kikuchi, E.; Ogura, M.; Aratani, N.; Sugiura, Y.; Hiromoto, S.; Yogo, K. *Catal. Today* **1996**, *27*, 35−40.
(253) Jímenez-López, A.; Rodríguez-Castellón, E.; Maireles-Torres, P.; Díaz, L.; Mérida-Robles, J. *Appl. Catal. A* **2001**, *218*, 295−306.
(254) Bagnasco, G.; Ciambelli, P.; Czaran, E.; Papp, J.; Russo, G. *Stud. Surf. Sci. Catal.* **1982**, *12*, 275.
(255) Rouchaud, J.; Fripiat, J. *Bull. Soc. Chim. Fr.* **1969**, *1*, 78.
(256) Howe, R. F.; Mimming, H. *Proc. 9th Int. Congr. Catal.* **1988**, *4*, 1585.
(257) Kubota, T.; Kumada, F.; Tominaga, H.; Kunugi, T. *Int. Chem. Eng.* **1973**, *13*, 539.
(258) Arai, H.; Yamashiro, T.; Kubo, T.; Tominaga, H. *Bull. Jpn. Petr. Inst.* **1976**, *18*, 39.
(259) Minachev, K. M.; Usachev, K. Y.; Isakov, I. Y.; Rodin, A. P.; Kalinin, V. P. *Izv. Akad. Nauk. SSSR. Ser. Khim* **1981**, *724*.
(260) Elleuch, B.; Naccache, C.; Ben Taarit, Y. *Stud. Surf. Sci. Catal.* **1984**, *19*, 139.
(261) Laniecki, M.; Karge, H. G. *Stud. Surf. Sci. Catal.* **1995**, *94*, 211−18.
(262) Joyner, R. 219th ACS National Meeting, San Francisco, 2000; p COLL-351.
(263) Armengol, E.; Corma, A.; García, H.; Primo, J. *Eur. J. Org. Chem.* **1999**, 1915−1920.
(264) Li, T.-S.; Duan, H.-Y.; Li, B.-Z.; Tewari, B. B.; Li, S.-H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 291−294.
(265) Suzuki, M.; Tsutsumi, K.; Tkahashi, H.; Saito, Y. *Zeolites* **1988**, *8*, 387−392.
(266) Butterworth: A. J.; Clark, J. H.; Walton, P. H.; Barlow, S. J. *Chem. Commun.* **1996**, 1859−1860.
(267) Sharpless, K. B.; Yudin, A. K., U. S. Pat. Appl. Publ., US 20010001798, 2001.
(268) Sharpless, K. B.; Rudolph, J., PCT Int. Appl., WO 9833786, 1998.
(269) Adam, W.; Saha-Moeller, C. R.; Weichold, O. *J. Org. Chem.* **2000**, *65*, 2897−2899.
(270) Neumann, R.; Wang, T.-J. *Chem. Commun.* **1997**, 1915−1916.
(271) Centi, G.; Perathoner, S.; Tonini, S. *Catal. Today* **2000**, *61*, 211−221.
(272) Barton, D. H. R.; Doller, D. *Pure Appl. Chem.* **1991**, *63*, 1567−76.
(273) Stavropoulos, P.; Celenligil-Cetin, R.; Tapper, A. E. *Acc. Chem. Res.* **2001**, *34*, 745−752.
(274) Gozzo, F. *J. Mol. Catal. A* **2001**, *171*, 1−22.
(275) Minisci, F.; Fontana, F. *Chim. Ind.* **1998**, *80*, 1309−1316.
(276) Barton, D. H. R.; Tingshen, L. *Tetrahedron* **1998**, *54*, 1735−1744.
(277) Barton, D. H. R.; Hu, B. *Pure Appl. Chem.* **1997**, *69*, 1941−1950.
(278) Barton, D. H. R. *Chem. Soc. Rev.* **1996**, *25*, 237−239.
(279) Perkins, M. J. *Chem. Soc. Rev.* **1996**, *25*, 229−236.
(280) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504−512.
(281) Alvaro, M.; Ferrer, B.; García, H.; Sanjuán, A. *Tetrahedron* **1999**, *55*, 11895−11902.
(282) Armengol, E.; Corma, A.; Fornés, V.; García, H.; Primo, J. *Appl. Catal. A* **1999**, *181*, 305−312.
(283) Sabater, M. J.; Corma, A.; Domenech, A.; Fornés, V.; García, H. *Chem. Commun.* **1997**, 1285−1286.
(284) Ogunwumi, S. B.; Bein, T. *Chem. Commun.* **1997**, 901−902.
(285) Wulff, H. P., DE 1249079, 1980.
(286) Abbenhuis, H. C. L.; Krijnen, S.; van Santen, R. A. *Chem. Commun.* **1997**, 331.
(287) Cativiela, C.; Fraile, J. M.; García, J. I.; Mayoral, J. A. *J. Mol. Catal. A* **1996**, *112*, 259.
(288) Fraile, J. M.; García, J. I.; Mayoral, J. A.; Vispe, E. *J. Catal.* **2001**, *204*, 146.
(289) Sheldon, R. A.; Van Doorn, J. A. *J. Catal.* **1973**, *31*, 427−37.
(290) Sheldon, R. A.; van Vliet, M. C. A. *Fine Chemicals through Heterogeneous Catalysis*; Wiley-VCH: Weinheim, 2001.
(291) Sheldon, R. A. *J. Mol. Catal.* **1980**, *7*, 107.
(292) Schneider, A.; Baiker, A. *Catal. Catal. Rev. Sci. Eng.* **1995**, *37*, 515.
(293) Klein, S.; Maier, W. F. *Angew. Chem. Int. Ed. Engl.* **1997**, *35*, 22230.
(294) Kochkar, H.; Figueras, F. *J. Catal.* **1997**, *171*, 420.
(295) Imamura, S.; Nakai, T.; Kanai, H.; Ito, T. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1261−6.
(296) Muller, C. A.; Schneider, M. S.; Mallat, T.; Baiker, A. *J. Catal.* **2000**, *192*, 448−451.
(297) Maschmeyer, T.; Klunduk, M. C.; Martin, C. M.; Shephard, D. S.; Thomas, J. M.; Johnson, B. F. G. *Chem. Commun.* **1997**, 1847−1848.
(298) Klunduk, M. C.; Thomas, J. M.; Johnson, B. F. G.; Maschmeyer, T. Book of Abstracts, 218th ACS National Meeting, New Orleans, Aug. 22−26, 1999, INOR-145.
(299) Corma, A.; Crocker, M.; Garcia, H.; Palomares, E. *Chem. Phys. Chem.* **2000**, *1*, 93−97.
(300) Krijnen, S.; Abbenhuis, H. C. L.; Hanssen, R.; van Hooff, J. M. C.; van Santen, R. A. *Angew. Chem.* **1998**, *110*, 374.
(301) Thomas, J. M.; Raja, R.; Sankar, R.; Bell, R. *Nature* **1999**, *398*, 227.
(302) Bennett, M. A.; Robertson, G. B.; Rokicki, A.; Wickramasinghe, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 7098−105.
(303) Bennett, M. A.; Jin, H.; Willis, A. C. *J. Organomet. Chem.* **1993**, *451*, 249−56.

(304) Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566−8.
(305) Benett, J. M.; Marcus, B. K. *Stud. Surf. Sci. Catal.* **1988**, *37*, 269.
(306) Borovik, V.; Vorotyntsev, V.; Golodets, G. *Ukr. Khim. Zh.* **1989**, *55*, 587−589.
(307) Corma, A.; Navarro, M. T.; Pérez-Pariente, J., ES 9301327, 1993.
(308) Corma, A.; Navarro, M. T.; Pérez-Pariente, J. *J. Chem. Soc. Chem. Commun.* **1994**, *147*.
(309) Blasco, T.; Corma, A.; Martínez, A.; Matínez-Escolano, P. *J. Catal.* **1998**, *168*, 23.
(310) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, *386*, 321.
(311) Koyano, K. A.; Tatsumi, T. *Chem. Commun.* **1996**, *2*, 145.
(312) Morey, M.; Davidson, A.; Stucky, G. *Microp. Mater.* **1996**, *6*, 99.
(313) Bagshaw, S. A.; Di Renzo, F.; Fajula, F. *Chem. Commun.* **1996**, *18*, 2209.
(314) Roberts, M. A.; Sankar, G.; Thomas, C. L.; Jones, R. H.; Du, H.; Chen, J.; Pang, W.; Xu, R. *Nature* **1996**, *381*, 401.
(315) Corma, A.; Domine, M. E.; Gaona, J. A.; Jorda, J. L.; Navarro, M. T.; Rey, F.; Pérez-Pariente, J.; Tsuji, J.; McCulloch, B.; Nemeth, L. T. *Chem. Commun.* **1998**, 2211.
(316) Corma, A.; Jorda, J. L.; Navarro, M. T.; Rey, F. *Chem. Commun.* **1998**, 1899.
(317) Suh, Y.; Kim, N.; Ahn, W.; Rhee, H. *J. Mol. Catal. A* **2001**, *174*, 249−254.
(318) Sheldon, R. A.; Wallau, M. A.; Arends, I. W. C. E.; Schuchardt, U. *Ac. Chem. Res.* **1998**, *31*, 485.
(319) Haanepen, M. J.; Elemans-Mehring, A. M.; van Hooff, J. M. C. *Appl. Catal. A* **1997**, *152*, 203.
(320) Vercrysse, K. A.; Klingeleers, D. M.; Colling, T.; Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1998**, *117*, 469.
(321) Corma, A.; Navarro, M. T.; Nemeth, L.; Renz, M. *Chem. Commun.* **2001**, 2190−2191.
(322) Lazar, K.; Chandwadkar, A. J.; Fejes, P.; Cejka, J.; Ramaswamy, A. V. *J. Radioanal. Nuclear Chem.* **2000**, *246*, 143−148.
(323) Chaudhari, K.; Das, T. K.; Rajmohanan, P. R.; Lazar, K.; Sivasanker, S.; Chandwadkar, A. J. *J. Catal.* **1999**, *183*, 281−291.
(324) Koyano, K.; Tatsumi, T. *Sogo Shikensho Nenpo* **1996**, *55*, 165−168.
(325) Das, T. K.; Chaudhari, K.; Chandwadkar, A. J.; Sivasanker, S. *J. Chem. Soc., Chem. Commun.* **1995**, 2495−6.
(326) Ziolek, M.; Sobczak, I.; Nowak, I.; Decyk, P.; Lewandowska, A.; Kujawa, J. *Micropor. Mesopor. Mater.* **2000**, *35−36*, 195−207.
(327) Lim, S.; Haller, G. L. *Appl. Catal. A* **1999**, *188*, 277−286.
(328) Hahiyama, T.; Morikawa, K.; Sharpless, K. B. *J. Org. Chem.* **1992**, *57*, 5067−5068.
(329) Boudali, L. K.; Ghorbel, A.; Amri, H.; Figueras, F. *C. R. Acad. Sci., Ser. IIc* **2001**, *4*, 67−72.
(330) Taramasso, M.; Perego, G.; Notari, B., US 4410501, 1983.
(331) Ingallina, P.; Clerici, M. G.; Rossi, L.; Bellussi, G. *Stud. Surf. Sci. Catal.* **1994**, *92*, 31.
(332) Clerici, M. G.; Ingallina, P. *Catal. Today* **1998**, *41*, 251.
(333) Perego, C.; Carati, A.; Ingallina, P.; Mantegazza, M. A.; Bellussi, G. *Appl. Catal. A* **2001**, *221*, 63.
(334) Esposito, A.; Neri, C.; Buonomo, F., US 4480135, 1984.
(335) Clerici, M. G.; Romano, U., EP 230949, 1987.
(336) Clerici, M. G.; Antossi, B.; Bellussi, G., EP 412596, 1990.
(337) Huybrechts, D. R. C., WO 90105126, 1990.
(338) Roffia, P.; Pandovan, M.; Moretti, E.; de Alberti, G., EP 208311, 1987.
(339) Reddy, R. S.; Reddy, J. S.; Kumar, R.; Kumar, P. *J. Chem. Soc., Chem. Commun.* **1992**, *84*.
(340) Sasidharan, M.; Raju, S. V. N.; Srinivasan, K. V.; Paul, V.; Kumar, R. *Chem. Commun.* **1996**, *129*.
(341) Notari, B. *Stud. Surf. Sci. Catal.* **1987**, *37*, 413.
(342) Vayssilov, G. N. *Catal. Rev. Sci. Eng.* **1997**, *39*, 209.
(343) Doménech, A.; Corma, A.; García, H.; Valencia, S. *Top. Catal.* **2000**, *11/12*, 401−407.
(344) Corma, A.; Garcia, H.; Navarro, M. T.; Palomares, E. J.; Rey, F. *Chem. Mater.* **2000**, *12*, 3068−3072.
(345) Lin, W.; Frei, H. *J. Am. Chem. Soc.* **2002**, *124*, 9292−9298.
(346) Bellussi, G.; Carati, A.; Clerici, M. G.; Maddinelli, G.; Millini, R. *J. Catal.* **1992**, *133*, 220.
(347) Sinclair, P. E.; Catlow, C. R. A. *Chem. Commun.* **1997**, *19*, 1881.
(348) Boccuti, M. R.; Rao, K. M.; Zecchina, A.; Leofanti, G.; Petrini, G. *Stud. Surf. Sci. Catal.* **1988**, *48*, 133.
(349) Reddy, J. S.; Kumar, R. *J. Catal.* **1991**, *130*, 440−446.
(350) Pei, G. W.; Zajac, G. W.; Kaduc, J. A.; Faber, J.; Boyanov, B. I.; Duck, D.; Fazzini, D.; Morrison, T. J.; Yang, D. S. *Catal. Lett.* **1993**, *21*, 333.
(351) Bordiga, S.; Coluccia, S.; Lamberti, C.; Marchese, L.; Zecchina, A.; Boscherini, F.; Buffa, f.; Genoni, F.; Leofanti, G.; Petrini, G.; Vlaic, G. *J. Phys. Chem.* **1994**, *98*, 4125.
(352) Geobaldo, F.; Bordiga, S.; Zecchina, A.; Giamello, E.; Leofanti, G.; Petrini, G. *Catal. Lett.* **1992**, *16*, 109.
(353) Clerici, M. G.; Ingallina, P. *J. Catal.* **1993**, *140*, 71.
(354) Talsi, E. P.; Dabushkin, D. E. *J. Mol. Catal. A.* **1996**, *106*, 179.
(355) Bellussi, G.; Carati, A.; Clerici, M. G.; Esposito, A.; Millini, R.; Buonomo, F., BE 1001038, 1989.
(356) Reddy, J. S.; Kumar, R.; Ratnasamy, P. *Appl. Catal.* **1990**, *58*, L1.
(357) Serrano, D. P.; Hong-Xin, L. *J. Chem. Soc., Chem. Commun.* **1992**, 745.
(358) Camblor, M. A.; Corma, A.; Martínez, A.; Pérez-Pariente, J. *Chem. Commun.* **1992**, 589.
(359) Camblor, M. A.; Corma, A.; Pérez-Pariente, J. *Zeolites* **1993**, *13*, 82.
(360) Camblor, M. A.; Corma, A.; Martínez, A.; Pérez-Pariente, J.; Valencia, S. In Influence of the synthesis procedure and chemical composition on the activity of titanium in titanium beta catalysts, *New Developments in Selective Oxidation II*; Cortés-Corberán, V., Vic-Bellón, S., Eds.; Elsevier: Amsterdam, 1994; Vol. 82, pp 531−540.
(361) Corma, A.; Camblor, M. A.; Esteve, P.; Martínez, A.; Pérez-Pariente, J. *J. Catal.* **1994**, *151*, 145.
(362) Corma, A.; Esteve, P.; Martínez, A.; Valencia, S. *J. Catal.* **1995**, *152*, 18.
(363) Blasco, T.; Camblor, M. A.; Corma, A.; Pérez-Pariente, J. *J. Am. Chem. Soc.* **1993**, *115*, 11806.
(364) Sato, T.; Dakka, J.; Sheldon, R. A. *Surf. Sci. Catal.* **1994**, *84*, 1853.
(365) Corma, A.; Iglesias, M.; Sánchez, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1635.
(366) Camblor, M. A.; Constantine, S.; Corma, A.; Esteve, P.; Gilbert, A.; Martínez, A.; Valencia, S. *Appl. Catal. A* **1995**, *133*, 2185.
(367) Camblor, M. A.; Corma, A.; Constantine, M.; Gilbert, A.; Gilbert, L.; Pérez-Pariente, J.; Valencia, S., FR 101823, 1995.
(368) Camblor, M. A.; Constantine, M.; Corma, A.; Gilbert, A.; Esteve, P.; Martínez, A.; Valencia, S. *Chem. Commun.* **1996**, 1339.
(369) van der Waal, J. C.; Lin, P.; Rigutto, M. S.; van Bekkum, H. *Stud. Surf. Sci. Catal.* **1997**, *105*, 1093.
(370) van der Waal, J. C.; Kunkeler, P. J.; Tan, K.; van Bekkum, H. *J. Catal.* **1998**, *173*, 74.
(371) Davis, R. J.; Liu, Z.; Tabora, J. E.; Wieland, W. S. *Catal. Lett.* **1995**, *34*, 101.
(372) Saxton, R. J.; Crocco, G. L.; Zajacek, J. G.; Wijesekea, K. S., EP 659685, 1994.
(373) van der Waal, J. C.; Rigutto, M. S.; van Bekkum, H. *Appl. Catal. A* **1998**, *167*, 331.
(374) Valencia, S.; Camblor, M. A.; Corma, A., SP 9600625, 1996.
(375) Blasco, T.; Camblor, M. A.; Corma, A.; Esteve, P.; Martínez, A.; Prieto, C.; Valencia, S. *Appl. Catal. A* **1996**, *167*, 331.
(376) Weitkamp, J.; Ernst, S.; Roland, E.; Thiele, G. F. *Stud. Surf. Sci. Catal.* **1997**, *105*, 763.
(377) Tangaraj, A.; Kumar, R.; Mirajkar, S. P.; Ratnasamy, P. *J. Catal.* **1991**, *130*, 129.
(378) Tuel, A.; ben Taarit, Y. *Zeolites* **1994**, *14*, 272.
(379) Blasco, T.; Camblor, M. A.; Corma, A.; Esteve, P.; Guil, J. M.; Martínez, A.; Perdigón-Melón, J. A.; Valencia, S. *J. Phys. Chem. B* **1998**, *102*, 77−88.
(380) Clerici, M. G.; Bellussi, G.; Romano, U. *J. Catal.* **1991**, *129*, 159.
(381) Shibata, M.; Gerard, J.; Gabelica, Z. *Microp. Mater.* **1997**, *12*, 141.
(382) Sastre, G.; Corma, A. *Chem. Phys. Lett.* **1999**, *302*, 447.
(383) Inamura, S.; Nakai, T.; Nakai, H.; Ito, T. *Catal. Lett.* **1994**, *28*, 277.
(384) Jänchen, J.; Vorbeck, G.; Stach, H.; Parltiz, B.; van Hoof, J. H. C. *Stud. Surf. Sci. Catal.* **1995**, *94*, 108.
(385) Muscas, M.; Solinas, V.; Gontier, S.; Tuel, A.; Auroux, A. *Stud. Surf. Sci. Catal.* **1995**, *94*, 101.
(386) Bittar, A.; Adnot, A.; Sayari, A.; Kaliaguine, S. *Res. Chem. Intermed.* **1992**, *18*, 49.
(387) Auroux, A.; Gervasini, A.; Jorda, E.; Tuel, A. *Stud. Surf. Sci. Catal.* **1994**, *84*, 653.
(388) Sasidharan, M.; Kumar, R. *Catal. Lett.* **1996**, *38*, 251.
(389) Inamura, S.; Nakai, H.; Nakai, T.; Ito, T. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1261.
(390) Tuel, A. *Zeolites* **1995**, 236.
(391) Villaescusa Alonso, L. A.; Camblor Fernandez, M. A., PCT Int. Appl., WO 0037360, 2000.
(392) Diaz-Cabanas, M.-J.; Villaescusa, L. A.; Camblor, M. A. *Chem. Commun.* **2000**, 761−762.
(393) Corma, A.; Díaz, U.; Dómine, M. E.; Fornés, V. *Angew. Chem., Int. Ed.* **2000**, *39*, 1499−1501.
(394) Corma, A.; Diaz, U.; Domine, M. E.; Fornes, V. *J. Am. Chem. Soc.* **2000**, *122*, 2804−2809.
(395) Corma, A.; Díaz-Cabañas, M. J.; Dómine, M. E.; Rey, F. *Chem. Commun.* **2000**, 1725−1726.
(396) Wu, P.; Komatsu, T.; Yashima, T.; Tatsumi, T. *Stud. Surf. Sci. Catal.* **2001**, *135*, 4375−4383.
(397) Sasidharan, M.; Wu, P.; Tatsumi, T. *J. Catal.* **2002**, *205*, 332−338.
(398) Corma, A.; Díaz, U.; Dómine, M. E.; Fornés, V. *Chem. Commun.* **2000**, 137−138.
(399) Perego, C.; Millini, R.; Bellussi, G. *Molecular Sieves Springer, Berlin* **1998**, *1*, 187.

(400) Rigutto, M. S. Ph.D. Dissertation, Delft University, 1994.
(401) Huybrechts, D. R. C.; Vaesen, I.; Jacobs, P. A.; Li, H. X. *Catal. Lett.* **1991**, *8*, 237.
(402) Adam, W.; Mitchell, C. M.; Saha-Moller, C. R.; Weichold, O.; Garcia, H. *Chem. Commun.* **1998**, 2609−2610.
(403) Adam, W.; Corma, A.; Garcia, H.; Weichold, O. *J. Catal.* **2000**, *196*, 339−344.
(404) Jacobson, S. E.; Muccigrosso, D. A.; Mares, F. *J. Org. Chem.* **1979**, *44*, 921.
(405) Esposito, A.; Maspero, F.; Romano, U. Proc. DGMK−Conf., Goslar, Germany, 1992; pp 195−204.
(406) Maspero, F.; Romano, U. *J. Catal.* **1994**, *146*, 476.
(407) Conte, V.; Di Furia, F. *Catalytic Oxidations with $H_2O_2$ as Oxidant*; Kluwer: Dordrecht, 1993.
(408) Schuster, W.; Niederer, J. P. M.; Hoelderich, W. F. *Appl. Catal. A* **2001**, *209*, 131−143.
(409) Huybrechts, D. R. C.; de Bruyker, L.; Jacobs, P. A. *Nature* **1990**, *345*, 240−2.
(410) Clerici, M. G. *Appl. Catal.* **1991**, *68*, 249−61.
(411) Mimoun, H.; Saussine, L.; Daire, E.; Porterl, M.; Fisher, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 310.
(412) Khouw, C. B.; Dartt, C. B.; Labinger, J. A.; Davis, M. E. *J. Catal.* **1994**, *149*, 195.
(413) Ramaswamy, A. V.; Sivansanker, S.; Ratnasamy, P. *Microp. Mater.* **1994**, *2*, 451.
(414) Huybrechts, D. R. C.; Buskens, P. L.; Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1992**, *72*, 21−31.
(415) Clerici, M. G. *Top. Catal.* **2001**, *15*, 257−263.
(416) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.
(417) Miyamoto, M.; Medhanavyn, D.; Unui, T. *Appl. Catal.* **1986**, *28*, 89.
(418) Rao, P. R.; Hari, P.; Kumar, R.; Ramaswamy, A. V.; Ratnasamy, P. *Zeolites* **1993**, *13*, 663−670.
(419) Rigutto, M. S.; van Bekkum, H. *Appl. Catal.* **1991**, *68*, 1L.
(420) Tuel, A.; Ben Taarit, Y. *Appl. Catal. A* **1993**, *102*, 201.
(421) Reddy, K. R.; Ramaswamy, A. V.; Ratnasamy, P. *J. Chem. Soc., Chem. Commun.* **1992**, 1613.
(422) Hari, P. R.; Rao, P.; Ramaswamy, A. V. *J. Chem. Soc., Chem. Commun.* **1992**, 1245−6.
(423) Centi, G.; Perathoner, S.; Trifiró, F.; Aboukais, A.; Aissi, C. F.; Guelton, M. *J. Phys. Chem.* **1992**, *96*, 2617.
(424) Hari, P. R.; Rao, P.; Belhekar, A. A.; Edge, S. J.; Ramaswamy, A. V.; Ratnasamy, P. *J. Catal.* **1993**, *141*, 595.
(425) Weckhuysen, B. M.; Baetens, D.; Schoonheydt, R. A. *Stud. Surf. Sci. Catal.* **2001**, *135*, 688.
(426) Das, N.; Eckert, H.; Hu, H.; Wachs, I. E.; Walzer, J.; Feher, F. *J. Phys. Chem.* **1993**, *97*, 8240.
(427) Eckert, H.; Wachs, I. E. *J. Phys. Chem.* **1989**, *93*, 6796.
(428) Kawai, M.; Kyora, T., **1993**, JP 0356439.
(429) Kawai, M.; Kyora, T., **1991**, JP 0358954.
(430) Sheldon, R. A.; Chen, J. D.; Dakta, J.; Neeleman, E. 11th World Congress on Selective oxidation, Benalmadena, Spain, 1994; p 61.
(431) van der Puil, N.; Jansen, J. C.; Van Bekkum, H. *Stud. Surf. Sci. Catal.* **1994**, *84A*, 210.
(432) Cornaro, U.; Jiru, P.; Tvaruzkova, Z.; Habersberger, K. *Stud. Surf. Sci. Catal.* **1991**, *69*, 165.
(433) Singh, P. S.; Bandyopadhyay, R.; Shaikh, R. A.; Rao, B. S. *Stud. Surf. Sci. Catal.* **1995**, *97*, 343−50.
(434) Novak Tusar, N.; Ristic, A.; Ghanbari-Siahkali, A.; Dwyer, J.; Mali, G.; Arcon, I.; Kaucic, V. *Stud. Surf. Sci. Catal.* **2001**, *135*, 2231−2238.
(435) Frunza, L.; Pelgrims, J.; Leeman, H.; van der Voort, P.; Vansant, E. F.; Schoonheydt, R. A. *J. Phys. Chem. B.* **2001**, *105*, 2677.
(436) Weckhuysen, B. M.; Rao, R. R.; Martens, J. A.; Schoonheydt, R. A. *Eur. J. Inorg. Chem.* **1999**, *4*, 565.
(437) Schoonheydt, R. A.; de Vos, R.; Pelgrims, J.; Leeman, H. *Stud. Surf. Sci. Catal.* **1989**, *37*, 269.
(438) Iton, L. E.; Choi, I.; Desjardins, J. A.; Maroni, V. A. *Zeolites* **1989**, *9*, 535.
(439) Montes, C.; Davis, M. E.; Murray, B.; Narayaua, M. *J. Phys. Chem.* **1990**, *94*, 6425.
(440) Kraushaar-Czarnetzki; Hoogervorst, W. G. M.; Andrea, R. R.; Emeis, C. A.; Stork, W. H. J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 891.
(441) Peeters, M. P. J.; van der Ven, L. J. M.; de Haan, J. W.; van Hoff, J. H. C. *Colloids Surf.* **1993**, *72*, 87.
(442) Barrett, P. A.; Sankar, G.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem.* **1996**, *100*, 8977−85.
(443) Gianotti, E.; Marchese, L.; Martra, G.; Coluccia, S. *Catal. Today* **1999**, *54*, 547−552.
(444) Gianotti, E.; Marchese, L.; Martra, G.; Coluccia, S. Proc. Int. Zeolite Conf., 12th, Baltimore, 1999; pp 2775−2780.
(445) Marchese, L.; Martra, G.; Damilano, N.; Coluccia, S.; Thomas, J. M. *Stud. Surf. Sci. Catal.* **1996**, *101*, 861−870.
(446) Costa, C. S.; Lourenco, J. P.; Henriques, C.; Antunes, A. P.; Ribeiro, F. R.; Ribeiro, M. F.; Gabelica, Z. Proc. Int. Zeolite Conf., 12th, Baltimore, 1999; pp 1771−1778.
(447) Montes, C.; Davis, M. E.; Murray, B.; Narayana, M. *J. Phys. Chem.* **1990**, *94*, 6431.
(448) Jhung, S. H.; Uh, Y. S.; Chon, H. *Appl. Catal.* **1990**, *62*, 61.
(449) Rigutto, M. S.; van Bekkum, H. *J. Mol. Catal.* **1993**, *81*, 77.
(450) Yu, X.; Maddox, P. J.; Thomas, J. M. *Polyhedron* **1989**, *8*, 819.
(451) Hocevar, S.; Batista, J.; Kaucic, V.; Cheetman, G. M. T.; Harding, M. M.; Kariuki, B. M.; Zizkallah, P. J. 9th Int. Zeol. Conf., Montreal, 1992.
(452) Chen, J. D.; Lempers, H. E. B.; Sheldon, R. A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1807−1813.
(453) Escalante, D.; Giraldo, L.; Pinto, M.; Pfaff, C.; Sazo, V.; Matjushin, M.; Mendez, B.; Lopez, C. M.; Machado, F. J.; Goldwasser, J.; Ramirez de Agudelo, M. M. *J. Catal.* **1997**, *169*, 176−187.
(454) Chen, J. D.; Sheldon, R. A. *J. Catal.* **1995**, *1−8*, 153.
(455) Tusar, N.; Logar, N.; Arcon, E.; Thibault-Starzyk, F.; Kaucic, V. *Croat. Chem. Acta* **2001**, *74*, 837−849.
(456) Rao, P.; Hari, P. R.; Belhekar, A. A.; Hegde, S. G.; Ramaswamy, A. V.; Ratnasamy, P. *J. Catal.* **1993**, *141*, 595−603.
(457) Mal, N. K.; Ramaswamy, A. V.; Ganapathy, S.; Ramaswamy, V. *J. Chem. Soc., Chem. Commun.* **1994**, 1933.
(458) Mal, N. K.; Bhaumik, A.; Kumar, R.; Ramaswamy, A. V. *Catal. Lett.* **1995**, *33*, 387.
(459) Fejes, P.; Nagy, J. B.; Kovacs, K.; G., V. *Appl. Catal. A* **1996**, *145*, 155.
(460) Mal, N. K.; Ramaswamy, V.; Rajamohanan, P. R.; Ramaswamy, A. V. *Stud. Surf. Sci. Catal.* **1997**, *12*, 331.
(461) Mal, N. K.; Ramaswamy, A. V. *Chem. Commun.* **1997**, 425.
(462) Li, J.; Kessler, H. *Mesopor. Mater.* **1999**, *27*, 57.
(463) Corma, A.; Nemeth, L. T.; Renz, M.; Valencia, S. *Nature* **2001**, *412*, 423.
(464) Renz, M.; Nagy, J. B.; Kovács, K.; Vankó, G. *Appl. Catal. A* **1996**, *145*, 155.
(465) Renz, M.; Blasco, T.; Corma, A.; Jensen, R.; Nemeth, L. T. *Chem. Eur. J.* **2002**, in press.
(466) Ito, S.; Omae, S., Jpn. Kokai Tokkyo Koho, JP 2001270873, 2001.
(467) Ito, S.; Seo, T., Jpn. Kokai Tokkyo Koho, JP 2001270880, 2001.
(468) Tsuji, J.; Oku, N., Jpn. Kokai Tokkyo Koho, JP 2001270878, 2001.
(469) Oku, N.; Omae, T., PCT Int. Appl., WO 0170715, 2001.
(470) Seo, T.; Tsuji, J., PCT Int. Appl., WO 0170714, 2001.
(471) Tsuji, J.; Omae, T., PCT Int. Appl., WO 0170711, 2001.
(472) Tsuji, J.; Yamamoto, J., PCT Int. Appl., WO 0170710, 2001.
(473) Thiele, G. F.; Roland, E. *J. Mol. Catal. A* **1997**, *117*, 351.
(474) Occhiello, E. *Chem. Ind.* **1997**, *6 October*, 761.
(475) Tatsumi, T.; Nakamura, M.; Negishi, S.; Tominaga, H. *J. Chem. Soc., Chem. Commun.* **1990**, 476.
(476) Corma, A.; Dómine, M. E.; Nemeth, L.; Valencia, S. *J. Am. Chem. Soc.* **2002**, *124*, 3194−3195.
(477) Camblor, M. A.; Corma, A.; Esteve, P.; Martínez, A.; Valencia, S. *Chem. Commun.* **1997**, 795.
(478) Huybrechts, D. R. C.; Buskens, P. L.; Mathys, G. M. K.; Martens, J. A., **1994**, WO 9402245.
(479) Cao, G. Y.; Li, H. Y.; Xia, Q. H.; Huang, J. S.; Xu, Y. D. *Cuihua Xuebao* **1995**, *16*, 217.
(480) Reddy, J. S.; Khire, U. R.; Ratnasamy, P.; Mitra, R. B. *J. Chem. Soc., Chem. Commun.* **1992**, 1234.
(481) Corma, A.; Fornés, V.; Pergher, S. B.; Maesen, T. L. M.; Buglass, J. G. *Nature* **1998**, *396*, 353−356.
(482) Tont, S.; Roffia, P.; Gervassutti, V., US 5227525, 1993.
(483) Cesana, A.; Mantegazza, M. A.; Pastori, M. *J. Mol. Catal. A* **1997**, *117*, 367.
(484) Kim, J. K.; Ko, Y. S.; Ann, W. S. *Kongop Hwahak* **1995**, *6*, 626.
(485) Bars, J. L.; Dakka, J.; Sheldon, R. A. *Appl. Catal.* **1996**, *136*, 69.
(486) Komatsu, T.; Yashima, T. *J. Catal.* **1997**, *168*, 400.
(487) Neri, C. S.; Costanzi, S.; Riva, R. M.; Angaroni, M., EP 488403, 1992.
(488) Horchler von Locquenghien, K.; Hölderich, W. F.; Baus, U.; Reuther, W.; Hahn, E., EP 567827, 1993.
(489) Gontier, S.; Tuel, A. *Appl. Catal.* **1994**, *118*, 173.
(490) Sonowane, H. R.; Pol, A. V.; Moghe, P. P.; Biswas, S. S.; Sudulai, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1215.
(491) Reni, J.; Sudalai, A.; Ravindranathan, T. *Synlett.* **1995**, 1177−8.
(492) Jorda, E.; Tuel, A.; Teissier, R.; Kervennal, J. Proc. Int. Zeolite Conf., 12th, Baltimore, 1999; pp 1269−1275.
(493) Reddy, J. S.; Jacobs, P. A. *Catal. Lett.* **1996**, *37*, 213−16.
(494) Kumar, P.; Hegde, V. R.; Pandey, B.; Ravindranathan, T. *J. Chem. Soc. Chem. Commun.* **1993**, 1553.
(495) Corma, A.; Iglesias, M.; Sanchez, F. *Catal. Lett.* **1996**, *39*, 153−156.
(496) Rabion, A.; Fajula, F.; Bernard, J.-R.; Hulea, V., **2001**, PCT Int. Appl., WO 0148119.
(497) Hulea, V.; Fajula, F.; Bousquet, J. *J. Catal.* **2001**, *198*, 179−186.
(498) Rafelt, J.; Clark, J. H. *Catal. Today* **2000**, *33*, 57.
(499) Clerici, M. G. *Fine Chemicals through Heterogeneous Catalysis*; Wiley-VCH: Weinheim, 2001.

(500) van der Pol, A. J. H. P.; Verduyn, A. J.; van Hoof, J. H. C. *Appl. Catal. A* **1993**, *99*, 71.
(501) Tuel, A.; Ben Taarit, Y. *Appl. Catal. A* **1993**, *102*, 69.
(502) Romano, U.; Esposito, A.; Maspero, F.; Neri, C.; Clerici, M. G. *Chim. Ind.* **1990**, *72*, 610.
(503) Tendulkar, B.; Tambe, S. S.; Chandra, I.; Rao, P. V.; Naik, R. V.; Kulkarni, B. D. *Ind. Eng. Chem. Res.* **1998**, *37*, 2091.
(504) Bhaumik, A.; Kumar, R. *J. Chem. Soc., Chem. Commun.* **1995**, *349*.
(505) Ferrini, C.; Kouwenhoven, H. W. *Stud. Surf. Sci. Catal.* **1990**, *55*, 53.
(506) Wu, P.; Komatsu, T.; Yashima, T. *J. Phys. Chem. B* **1998**, *102*, 9297.
(507) Kim, G. J.; Cho, B. R.; Kim, J. H. *Catal. Lett.* **1993**, *22*, 259.
(508) Bhelhekar, A. A.; Das, T. K.; Chaudhuri, K.; Hegde, S. G.; Chandwadkar, J. *Stud. Surf. Sci. Catal.* **1998**, *113*, 195.
(509) Kumar, R.; Bhaumik, A. *Microp. Mesop. Mater.* **1998**, *21*, 497.
(510) Henrik, C. A., US 5648562 8, 1997.
(511) Adam, W.; Corma, A.; Reddy, T. I.; Renz, M. *J. Org. Chem.* **1997**, *62*, 3631−3637.
(512) Adam, W.; Corma, A.; Martinez, A.; Mitchell, C. M.; Reddy, T. I.; Renz, M.; Smerz, A. K. *J. Mol. Catal. A* **1997**, *117*, 357−366.
(513) Corma, A.; Esteve, P.; Martinez, A. *Appl. Catal. A* **1996**, *143*, 87−100.
(514) Corma, A.; Esteve, P.; Martinez, A. *J. Catal.* **1996**, *161*, 11−19.
(515) Bellussi, G.; Rigutto, M. S. *Stud. Surf. Sci. Catal.* **1994**, *85*, 177.
(516) Hutchings, G.; Lee, D. F. *J. Chem. Soc., Chem. Commun.* **1994**, 1095−6.
(517) Davies, L. J.; McMorn, P.; Bethell, D.; Page, P. C. B.; King, F.; Hancock, F. E.; Hutchings, G. J. *J. Mol. Catal. A* **2001**, *165*, 243−247.
(518) Hutchings, G. J.; Lee, D. F.; Minihan, A. R. *Catal. Lett.* **1996**, *39*, 83−90.
(519) Hutchings, G. J.; Lee, D. F.; Minihan, A. R. *Catal. Lett.* **1995**, *33*, 369−85.
(520) Neuman, R.; Levin-Elad, M. *Appl. Catal. A* **1995**, *122*, 85.
(521) Lempers, H. E. B.; Sheldon, R. A. *J. Catal.* **1998**, *175*, 62.
(522) Peeters, M. P. J.; Busio, M.; Leyten, P.; van Hoff, J. H. C. *Appl. Catal. A* **1996**, *118*, 8977.
(523) Vanoppen, D. L.; De Vos, D. E.; Genet, M. J.; Rouxhet, P. G.; Jacobs, P. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 560.
(524) Mal, N. K.; Ramaswamy, A. V. *J. Mol. Catal. A* **1996**, *105*, 149.
(525) Ooi, T.; Ichikawa, H.; Markova, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 3610.
(526) Shabtai, J.; Lazar, R.; Biron, E. *J. Mol. Catal.* **1984**, *27*, 35.
(527) Huang, M.; Zielinski, P. A.; Moulod, J.; Kaliaguine, S. *Appl. Catal. A* **1994**, *118*, 33.
(528) Berkani, M.; Lemberton, J. L.; Marczewski, M.; Perot, G. *Catal. Lett.* **1995**, *31*, 405.
(529) Creyghton, E. J.; Ganeshie, S. D.; Dowing, R. S.; Van Bekkum, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1859.
(530) van der Waal, J. C.; Tan, K.; van Bekkum, H. *Catal. Lett.* **1966**, *41*, 63.
(531) Kunkeler, P. J.; Zuurdeeg, B. J.; Van Der Waal, J. C.; van Bokhoven, J. A.; Koningsberger, D. C.; Van Bekkum, H. *J. Catal.* **1998**, *180*, 234.
(532) Corma, A.; Domine, M. E.; Jacquot, R., 2002, French Application.
(533) Sandee, A. J.; Petra, D. G. I.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Eur. J.* **2001**, *7*, 1202.
(534) Kustov, L. M.; Tarasov, A. L.; Bogdan, V. I.; Tyrlov, A. A.; Fulmer, J. W. *Catal. Today* **2000**, *61*, 123−128.
(535) Kustov, L.; Bodgan, V.; Kazanski, V., EU 98−305192, 1999.
(536) Gubelmann, M.; Tirel, J. P., EU 0341165, 1989.
(537) Gubelmann, M.; Tirel, P. J., US 5001280, 1991.
(538) Kharitonov, A. S.; Gennadii, I. P.; Kazimira, G. I.; Vyacheslav, N. R.; Galina, A. S.; Lidia, A. V.; Vladimir, I. S., US 5110995, 1992.
(539) Kharitonov, A. S.; Panov, G. I.; Sheveleva, G. A.; Pirutko, L. V.; Voskresenskaya, T. P.; Sobolev, V. I., WO 95/27560, 1995.
(540) Sheveleva, G. A.; Kharitonov, A. S.; Panov, G. I.; Sobolev, V. I.; Razdobarova, N. L.; Paukstis, E. A.; Romannikov, V. N. *Neftekhimiya* **1993**, *33*, 530−7.
(541) Selli, E.; Isernia, A.; Forni, L. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3301−3305.
(542) Mcghee, W., WO 98/07516, 1998.
(543) Rodkin, M. A.; Uriarte, A. K.; Sobolev, V. I.; Panov, G. I., WO 98/43934, 1998.
(544) Mcghee, W.; Notte, P., WO 98/07513, 1998.
(545) Perkins, M. J. *Chem. Soc. Rev.* **1996**, *25*, 229−236.
(546) Iglesia, E. *Preprints of Symposia − American Chemical Society, Division of Fuel Chemistry* **2002**, *47*, 128−131.
(547) Stahl, S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2181−2192.
(548) Parkyns, N. D. *Chem. Br.* **1990**, *26*, 841−4.
(549) Emig, G. *Chem. Ing. Technol.* **1977**, *49*, 865−73.
(550) Thomas, J. M.; Raja, R.; Sankar, G.; Johnson, B. F. G.; Lewis, D. W. *Chem. Eur. J.* **2001**, *7*, 2973−2978.
(551) Labinger, J. A.; Bercam, J. E. *Nature* **2002**, *417*, 507−514.
(552) Armengol, E.; Cano, M. L.; Corma, A.; García, H.; Navarro, M. T. *J. Chem. Soc., Chem. Commun.* **1995**, 519−520.
(553) Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515.
(554) Wang, J. Y.; Xia, G. G.; Yin, Y. G.; Suib, S. L.; Young, S. L. *J. Catal.* **1998**, *176*, 275.
(555) Ernst, S.; Selle, M. *Microp. Mesop. Mater.* **1999**, *27*, 355.
(556) Corma, A. *Chem. Rev.* **1997**, *97*, 2373−2419.
(557) Mizuno, N.; Nozaki, C.; Kiyoto, I.; Misono, M. *J. Am. Chem. Soc.* **1998**, *120*, 9267.
(558) Sabater, M. J.; Corma, A.; Folgado, J. V.; García, H. *J. Phys. Org. Chem.* **2000**, *13*, 57−62.
(559) Nozaki, C.; Misono, M.; Mizuno, N. *Chem. Lett.* **1998**, 1263−1264.
(560) Lyons, J. E.; Ellis, P. E.; Myers, W. K. *J. Catal.* **1995**, *155*, 59.
(561) Hayashi, T.; Kishida, A.; Mizuno, K. *Chem. Commun.* **2000**, *381*.
(562) Raja, R.; Ratnasamy, P., **1998**, US 5767320.
(563) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* **1991**, *1*, 1−4.
(564) Strukul, G. *Angew. Chem., Int. Ed. Engl.* **1998**, *39*, 1198.
(565) Raja, R.; Sankar, G.; Thomas, J. M. *Chem. Commun.* **1999**, 829.
(566) Raja, R.; Thomas, J. M.; Sankar, G. *Chem. Commun.* **1999**, 525.
(567) Deremince, V.; Vogels, C., US 5342603, 1994.
(568) McAdam, J.; Sankey, J. P.; Wilson, K., WO 9407855, 1994.
(569) Clerici, M. G.; Ingallina, P., US 5221795 and 5252758, 1993.
(570) Rodriguez, C. L.; Zajacek, J. C., US 5463090, 1995.
(571) Nijhuis, T. A.; Huzinga, B. J.; Makkee, M.; Moulijn, J. *Ind. Eng. Chem. Res.* **1999**, *38*, 884.
(572) Zatorski, L. W.; Centi, G.; López-Nieto, J. M.; Trifiro, F.; Bellussi, G.; Fattose, V. *Stud. Surf. Sci. Catal.* **1989**, *49B*, 1243.
(573) Bellussi, G.; Centi, G.; Perathoner, S.; Trifiro, F. *ACS Symp. Ser.* **1993**, *523*, 281.
(574) Chen, J. D.; Dakka, J.; Sheldon, R. A.; Neelemand, J. *Chem. Commun.* **1993**, 1379.
(575) Thomas, J. M. *Top. Catal.* **2001**, *15*, 85.
(576) Belkhir, I.; Germanin, A.; Fajula, F.; Fache, E. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1761.
(577) Raja, R.; Sankar, G.; Thomas, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 11926.
(578) Thomas, J. M.; Raja, R.; Sankar, G.; Bell, R. G. *Acc. Chem. Res.* **2001**, *34*, 191.
(579) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1993**, *115*, 7501−7502.
(580) Blatter, F.; Moreau, F.; Frei, H. *J. Phys. Chem.* **1994**, *98*, 13403−13407.
(581) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812−1820.
(582) Sun, H.; Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 7951−7952.
(583) Sun, H.; Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1996**, *118*, 6873−6879.
(584) Vasenkov, S.; Frei, H. *J. Phys. Chem. B* **1998**, *102*, 8177−8182.
(585) Vasenkov, S.; Frei, H. In *Photooxidation in Zeolites*, *Molecular and Supramolecular Photochemistry*; Schanze, V., Ramamurthy, V., Eds.; Wiley: New York, 2000; Vol. 5, pp 295−323.
(586) Vanoppen, D. L.; Devos, D. E.; Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1997**, *105*, 1045−1051.
(587) Tao, Y.-W.; Zhong, S.-H. *Fenzi Cuihua* **2000**, *14*, 327−331.
(588) Zhong, S.; Gao, F.; Ye, W.; Xiao, X. *Wuli Huaxue Xuebao* **2000**, *16*, 601−607.
(589) Zhong, S.-H.; Gao, F.; Ye, W.-Q.; Xiao, X.-F. *Yingyong Huaxue* **2000**, *17*, 238−242.
(590) Rao, Y. V. S.; De′vos, D. E.; Wouters, B.; Grobet, P. J.; Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1997**, *110*, 973−980.
(591) Chisem, I. C.; Rafelt, J.; Shieh, M. T.; Chisem, J.; Clark, J. H.; Jachuck, R.; Macquarrie, D. J.; Scott, K. *Chem. Commun.* **1998**, 1949−1950.
(592) Dean, J. A. *Lange's Handbook of Chemistry*; 14th ed.; McGraw-Hill: New York, 1992.
(593) Jorgenson, K. A. *Chem. Rev.* **1989**, *89*, 431.
(594) Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566.
(595) Uphade, B. S.; Okumura, M.; Tsubota, S.; Maruta, M. *Appl. Catal.* **1989**, *186*, 288.
(596) Bowman, R. G.; Maj, J. I.; Clark, H. W.; Hartwell, G. E.; Womack, J. L.; Bare, S. R., WO 98/00414, 1998.
(597) Haruta, M.; Angelov, K. J.; Tsubota, T.; Hatashi, T.; Wada, M., JP 11128743, 1999.
(598) Schulz, R. P.; Dingerdissen, U.; Orzekek, M.; Maier, W., DE 19754303, 1999.
(599) Weisbeck, M.; Dorf, E.; Wegener, G.; Schild, C.; Lucke, B.; Dilcher, H.; Schulke, W., WO 99/40077, 1999.
(600) Kolombos, A. J.; McCain, C. C., UK 1327497, 1973.
(601) Thorsteinson, E. M., CA 1282772, 1991.
(602) Bowman, R. G., US 4845253, 1989.
(603) Lu, G.; Zno, X. *Catal. Lett.* **1999**, *58*, 67.
(604) Gaffney, A. M.; Jones, C. A.; Pitchai, R.; Kahn, A. P., US 5698719, 1997.
(605) Pitchai, R.; Kahn, A. P.; Gaffney, A. M., US 5686380, 1997.
(606) Gaffney, A. M.; Kahn, A. P.; Pitchai, R., US 5703254, 1997.
(607) Cooker, B.; Gaffney, A. M.; Jewson, J. D.; Kahn, A. P.; Pitchai, R., US 5770746, 1998.

(608) Cooker, B.; Gaffney, A. M.; Jewson, J. D.; Khan, A. P.; Onimus, W. H., US 5780657, 1980.
(609) Monnier, J. R. *Stud. Surf. Sci. Catal.* **1997**, *110*, 135.
(610) Monnier, J. R. *App. Catal. A* **2001**, *221*, 73.
(611) Monnier, J. R.; Muelhlbauer, P. J., US 4897498, 1990.
(612) Monnier, J. R.; Muelhlbauer, P. J., US 5138077, 1992.
(613) Stavinoha, J. L.; Monnier, J. R.; Hitch, D. M.; Nolen, T. R.; Oltean, G. L., US 5362890, 1994.
(614) Oltean, G. L.; Monnier, J. R., US 5908942, 1999.
(615) Barnicki, S. D.; Monnier, J. R.; Peters, K. T., US 5945550, 1999.
(616) Barnicki, S. D.; Monnier, J. R., US 6011163, 2000.
(617) *Chemical Week*, June 5, 1996.
(618) Linke, D.; Wolf, D.; Baerns, M.; Zeyss, S.; Dingerdissen, U.; Mleczko, L. *Chem. Eng. Sci.* **2002**, *57*, 39−51.
(619) Sano, K.-I.; Uchida, H.; Wakabayashi, S. *Catal. Surv. Jpn.* **1999**, *3*, 55−60.
(620) Blum, P. R.; Lemanski, M. F.; Hazen, J. B., SP 490507, 1992.
(621) Lu, G.; Huang, G.; Guo, Y.; Wang, R.; Bai, Q.; Li, C.; Qi, H. *Shiyou Huagong* **1985**, *14*, 262−6.
(622) Hallet, C. P., SP 480594, 1992.
(623) Kits, M., US 896904, 1992.
(624) Barthe, P.; Blanchard, G., SP 479692, 1992.
(625) Blum, P. R.; Papera, M. A., US 5300682, 1994.
(626) Mandal, S.; Kumar, N.; Varshney, U.; Bhattacharya, S. *J. Inorg. Biochem.* **1996**, *63*, 265−272.
(627) Zago, M.; Oteiza, P. *Free Radical Biol. Med.* **2001**, *31*, 266−274.
(628) Buetner, G. *J. Biochem. Biophys. Methods* **1988**, *16*, 27−40.
(629) Yoshino, S.; Suyiban, S.; Stern, A. *Arch. Biochem. Biophys.* **1989**, *272*.
(630) Neuzil, J.; Thomas, S.; Stocker, R. *Free Radical Biol. Med.* **1996**, *22*, 57−81.
(631) Pugia, M., EP96−107334, 1996.
(632) Mahadev, N.; Lumpkin, J. 211th ACS National Meeting, New Orleans, 1996; p BIOT-072.
(633) Dikalov, S.; Vitek, M.; Maples, K.; Mason, R. *J. Biol. Chem.* **1999**, *274*, 9392−9399.
(634) Krishnamurthy, R.; Madurawe, R.; Bush, K.; Lumpkin, J. *Biotechnol. Prog.* **1995**, *11*, 643−650.
(635) Ohno, A.; Oda, S.; Ishikawa, Y.; Yamazaki, N. *J. Org. Chem.* **2000**, *65*, 6381−6387.
(636) Wright, P. A.; Thomas, J. M.; Cheetham, A. K.; Novak, A. K. *Nature* **1985**, *318*, 611.
(637) Derouane, E. G. *J. Catal.* **1986**, *100*, 541.
(638) Parton, F. R.; Vankelecom, I. F. J.; Casselman, M. J. A.; Bezoukhanova, C. P.; Uytterhoeven, J. B.; Jacobs, P. A. *Nature* **1994**, *370*, 541.
(639) Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 913.
(640) Kessissoglou, D. P. *NATO ASI Ser., Ser. C* **1995**, *459*, 299−320.
(641) Muh, U.; Cinkaya, I.; Albracht, S. P.; Buckel, W. *Biochem.* **1996**, *35*, 11710−8.
(642) Singh, N.; Lee, D. G. *Org. Process Res. Dev.* **2001**, *5*, 599−603.
(643) Hypolito, R.; Valarelli, J. V.; Netto, S. M.; Guttler, R. S. *Geochim. Bras.* **1997**, *11*, 207−211.
(644) Taji, A.; Nishio, H.; Chifuku, H., **1997**, Jpn. Kokai Tokkyo Koho, JP09057263.
(645) Vella, P.; Veronda, B.; Vlastnik, E. *WEF/Purdue Ind. Wastes Conf.* **1999**, 281−298.
(646) Fickek, K. J.; Waer, M. A. *Proc. Natl. Conf. Drinking Water, 5th* **1993**, 205−19.
(647) Tabakov, D.; Shishkov, A. *Khim. Ind.* **1986**, *58*, 201−5.
(648) Vella, P. A.; Deshinsky, G.; Boll, J. E.; Munder, J.; Joyce, W. M. *Res. J. Water Pollut. Control Fed.* **1990**, *62*, 907−14.
(649) Garshina, S. I.; Prokopenkova, L. V.; Tararykov, G. M.; Perelygin, V. M. *Fermentn. Spirt. Prom-st.* **1977**, 13−15.
(650) Feikes, L.; Schroeder, D.; Reyer, P., **1985**, Ger. Offen., DE−3335746.
(651) Miyahara, S.; Kamiguchi, T.; Hashimukai, M.; Nitsuta, K., **1987**, Jpn. Kokai Tokkyo Koho, JP62262727.
(652) Moes, M.; Peabody, C.; Siegrist, R.; Urynowicz, M. *2nd Int. Conf. Rem. Chlorinated Recalcitrant Compd.* **2000**, 117−124.
(653) Kojima, Y.; Yoon, S.-L. *Polpu, Chongi Gisul* **2001**, *33*, 73−79.
(654) Stajic, V. M.; Jovancicevic, B. S.; Vitorovic, D. K. *Hem. Ind.* **1998**, *52*, 116−120.
(655) Lee, D. G.; Chen, T.; Wang, Z. *J. Org. Chem.* **1993**, *58*, 2918−19.
(656) Wang, B.; Burau, R. G. *Environ. Sci. Technol.* **1995**, *29*, 1504−10.
(657) Kapran, A. Y.; Solov′ev, S. A.; Vlasenko, V. M. *Theor. Exp. Chem.* **2000**, *36*, 94−97.
(658) Shen, Y. F.; Zerger, R. P.; DeGuzman, R. N.; Suib, S. L.; McCurdy, L.; Potter, D. I.; O′Young, C. L. *Science* **1993**, *260*, 511−15.
(659) Son, Y.-C.; Makwana, V. D.; Howell, A. R.; Suib, S. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4280−4282.
(660) Richter, M.; Trunschke, A.; Bentrup, U.; Brzezinka, K.-W.; Schreiber, E.; Scheneider, M.; Pohl, M.-M.; Fricke, R. *J. Catal.* **2002**, *206*, 98−113.
(661) Pasiuk-Bronikowska, W.; Rudzinski, K.; Bronikowski, T.; Ziajka, J. *Transp. Chem. Transform. Pollut.* **1996**, *2*, 116−125.
(662) Grgic, I.; Dovzan, A.; Bercic, G.; Hudnik, V. *J. Atmos. Chem.* **1998**, *29*, 315−337.
(663) Ghio, A.; Stonehuerner, J.; Perichard, R.; Piantadosi, C.; Quigly, D.; Breher, K.; Costa, D. *Inhalation Toxicol.* **1996**, *8*, 479−494.
(664) Rudyak, S.; Subolava, N.; Solozhenko, E. *Khim. Tekhnol. Voey* **1988**, *10*, 390−392.
(665) Thompson, F. E.; Sharratt, P. N.; Hutchison, J. *Eur. Conf. Young Res. Chem. Eng.* **1996**, *2*, 651−653.
(666) Bull, R., Patent, US 87−68371, 1988.
(667) Ledon, H.; Zumbrunn, J.; Cocolios, P.; Bron, P.; Campo, P.; Berthet, L., Patent, EP 262054, 1988.
(668) Bartmann, M.; Burzin, K.; Bevers, K., Patent, DE 84−3419601, 1985.
(669) Abma, W. R.; Buisman, C. J. N., Patent, EP 98−200950, 1999.
(670) Matacotta, F.; Calestani, G.; Cavani, F.; Fornasari, G., Patent, WO97−28887, 1997.
(671) Sinquin, G.; Petit, C.; Libs, S.; Hindermann, J. P.; Kiennemann, A. *Appl. Catal. B* **2001**, *32*, 37−47.
(672) Haber, J.; Machej, T.; Derewinski, M. X.; Janik, R.; Krysciak, J.; Sadowska, H.; Janas, J. *Catal. Today* **1999**, *54*, 47−55.
(673) Haber, J.; Machej, T.; Derewinski, M.; Janik, R.; Krysciak, J.; Sadowska, H. *Stud. Surf. Sci. Catal.* **1999**, *121*, 99−104.
(674) Levesque, S.; Yang, Y.; Larachi, F.; Sayari, A. Proc. Int. Zeolite Conf., 12th, Baltimore, 1998; pp 2869−2874.
(675) Larachi, F.; Levesque, S.; Sayari, A. *J. Chem. Technol. Biotech.* **1998**, *73*, 127−130.
(676) Otsuji, K.; Hidaya, M., Patent, JP 98−40841, 1999.
(677) Segal, S. R.; Cao, L.; Suib, S. L.; Tang, X.; Satyapal, S. *J. Catal.* **2001**, *198*, 66−76.
(678) Das, S.; Mandal, P. C.; Rath, M. C.; Mukherjee, T. *Res. Chem. Interm.* **1999**, *25*, 379−391.
(679) Legrini, O.; Oliveros, E.; Braun, A. M. *Chem. Rev.* **1993**, *93*, 671−698.
(680) Ollis, D. F.; Al-Ekabi, H. *Photocatalytic Purification and Treatment of Water and Air*; Elsevier: Amsterdam, 1993.
(681) Zhuang, J.; Rusu, C. N.; Yates, J. T., Jr. *J. Phys. Chem. B* **1999**, *103*, 6957−6967.
(682) Ikeda, S.; Sugiyama, N.; Pal, B.; Marci, G.; Palmisano, L.; Noguchi, H.; Uosaki, K.; Ohtani, B. *Phys. Chem. Chem. Phys.* **2001**, *3*, 267−273.
(683) Tae Kwon, Y.; Yong Song, K.; In Lee, W.; Jin Choi, G.; Rag Do, Y. *J. Catal.* **2000**, *191*, 192−199.
(684) Bull, R., Patent, EP 116536, 1990.
(685) Yamaguchi, H.; Yaguchi, T., Patent, JP10292278, 1998.
(686) Yaguchi, T.; Yamaguchi, H.; Wakai, M.; Yamagami, K., JP 08209573A2, 1996.
(687) Eremich, S.; Pruszynska, E., Patent, 1998.
(688) Smith, J.; Ellenor, D.; Harbinson, J., Patent, US 5,500,130, 1996.
(689) Smith, J.; Ellenor, D.; Harbinson, J., Patent, US 5,342,421, 1996.
(690) Svinova, L.; Astanina, A.; Rudenko, A. *Vestn. Mosk. University Ser. 2* **1989**, *30*, 193−196.
(691) Anderev, A.; Prahov, L.; Gadrovska, M.; Elyas, A.; Ivanova, V. *Appl. Catal. B* **1996**, *8*, 355−373.
(692) Mimoun, H.; Saussine, L.; Bonnaudt, S.; Robine, A.; Franck, J., Patent, FR 2588265, 1987.
(693) Zosimov, A.; Lounin, V.; Maximov, J., Patent, WO 97 35945, 1997.
(694) Nagai, M.; Goto, Y.; Ishii, H.; Omi, S. *Appl. Catal. A* **2000**, *192*, 189−199.
(695) Somani, S. M. *Chemical Warfare Agents*; Academic: San Diego, 1992.
(696) Yang, Y.-C. *Acc. Chem. Res.* **1999**, *32*, 109.
(697) Marques, A.; Marin, M.; Ruasse, M.-F. *J. Org. Chem.* **2001**, *66*, 7588−7595.
(698) Khorunzhii, B.; Motko, S. *Zh. Prikl. Khim.* **1985**, *58*, 237−242.
(699) Pinnavaia, T.; Amarasekera, J., Patent, US 5,219,536, 1994.
(700) Toshiba, JP 6061037, 1985.
(701) Toshiba, JP 6061036, 1985.
(702) Li, M.; Shen, J.; Ge, X.; Chen, X. *Appl. Catal., A* **2001**, *206*, 161−169.
(703) Elson, J.; Yoshpa, M., Patent, US 5,415,809, 1995.
(704) Blum, H.; Mayer, B.; Pegelow, U., Patent, DE 96−19620267, 1997.
(705) Speckmann, H.; Nitsch, C.; Blum, H., Patent, WO 0142417, 2001.
(706) Blum, H.; Speckmann, H.; Nitsch, C.; Lietzmann, A., Patent, DE 14925511, 2000.
(707) Gruetzke, J.; Schmidt, S., Patent, DE 9444432621, 1996.
(708) Han, S.; Jung, K.; Joo, O.; Cho, S.; Oh, J., **2001**, Patent, DE 10049545.
(709) Hojo, H., Patent, EP 95−108640, 1995.
(710) Chattopadhyay, A. K.; Sen, S. N.; Seshan, S.; Samanta, N. K.; Bhowmic, K. P., IN 86-CA390, 1990.
(711) Barnes, M.; Hock, C.; Cox, M.; Taylor, R.; Jordan, M.; Ward, A., Patent, EP 767155, 1997.
(712) Hock, C.; Jordan, M.; Chandler, V.; Taylor, R.; Deppert, T.; Barnes, M., EP 659715, 1995.
(713) Tatlor, R.; Deppert, T.; Barnes, M., US 5467715, 1995.

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