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Ordered Mesoporous and Microporous Molecular Sieves Functionalized with Transition Metal Complexes as Catalysts for Selective Organic Transformations

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I. Introduction

Immobilization of catalysts on inorganic matrices has several important potential advantages over other approaches such as the use of organic polymer supports. The chemical stability of the inorganic supports is important, particularly with regard to oxidizing conditions. Their mechanical stability is often excellent, since the issue of swelling depending on solvent conditions can largely be avoided. Finally, inorganic supports have superior thermal stability. The preparation of highly dispersed inorganic materials is now a mature technology, and crystalline or noncrystalline materials with controlled particle dimension, pore diameter, and dimensionality are available.

In the class of microporous materials, zeolites and related materials such as aluminophosphates have found for a long time applications outside the traditional areas of acid and bifunctional catalysis.[1] With the advent of the ordered micelle-templated inorganic materials, the choice of available supports has been considerably extended into the mesoporous domain. Examples are materials such as MCM-41, MCM-48, MSU, HMS, FSM-16, and various SBA type materials.[2] The distinction between these materials is based on the mechanisms involved in the synthesis, the pH conditions and the templates used, the topology, and the pore architecture. Popular templates are long-chain alkylammonium detergents, for the M41S family, including the hexagonal MCM-41 and the cubic MCM-48, long aliphatic amines, for HMS materials, and poly(ethylene oxide) surfactants and copolymers, for MSU and some SBA-type materials. In homogeneous catalyst immobilization, mesoporous materials with an all-SiO_2 or silica−alumina composition have mostly been applied, but in principle many more elemental compositions, including ordered mesoporous Al, Zr, Ti, ... oxides are available.[2b,3] If ordered mesoporous materials are used as catalyst supports, it may be desirable to improve or tune

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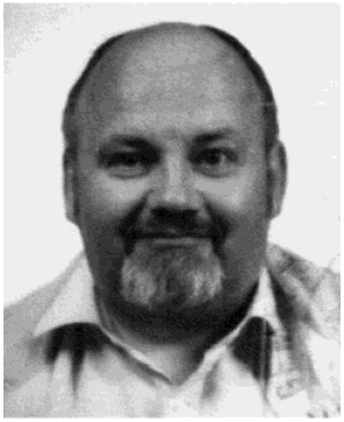
Dirk E. De Vos (°Mechelen, Belgium, 1967) obtained his Ph.D. degree in the group of Pierre Jacobs with a thesis on intrazeolite synthesis of metal complexes. He studied Mn oxidation catalysis in postdoctoral work with Thomas Bein at Purdue University. After returning to Leuven, he became an Associate Professor and teaches phytopharmaceutical chemistry and colloid chemistry. His research focuses on solid catalysts for organic transformations. Awards include the Breck award (1998) and the BASF award for Catalysis (2001).

Mieke Dams (°Geel, Belgium, 1977) finished her Master's thesis at the University of Leuven in Pierre Jacobs' group and is currently preparing a Ph.D. thesis in the domain of catalytic Heck and Suzuki reactions.

certain characteristics, for instance, the hydrothermal stability or wall thickness, or the polarity of the surface. Both thermal pretreatment and surface functionalization with silylating agents can change the surface hydrophobicity. Recently, the borderline between zeolites and mesoporous materials has become less sharp. First, some mesoporous materials apparently have micropores in the walls of the mesopores.[4] Second, materials have been prepared in which zeolite building blocks or small zeolite particles are arranged in a micelle-templated process to make up a mesoporous structure with microporous pore walls.[5]

As will be demonstrated by the examples in this review, there are many strategies for immobilization of metal complexes on ordered porous inorganic matrices. Simple physisorption is in several cases sufficient for retention of the metal complex. The ion-exchange capacity or the cage structure of zeolites can be exploited to immobilize metal complexes via electrostatic interactions or by entrapment. Finally covalent attachment of organic ligands to the microporous or mesoporous support, particularly via Si-alkoxide chemistry, is a popular and broadly applicable approach.

Bert F. Sels (°Mol, Belgium, 1972) graduated from the University of Leuven and stayed for doctoral and postdoctoral work in the group of Pierre Jacobs. His Ph.D. thesis focused on peroxide reactions with LDH-derived catalysts. For his work, he was awarded several prizes, including the DSM award for Chemistry and Technology (1999).



Pierre A. Jacobs (°Gooik, Belgium, 1943) is the head of the Department Interphase Chemistry of the K. U. Leuven, Belgium. His research started in physical chemistry of zeolite catalysts, with a Ph.D. thesis under the direction of Jan Uytterhoeven. He pioneered hydrocarbon reactions with zeolites, and then gradually took an interest in heterogeneous catalysis applied to the synthesis of fine chemicals. He is a former president of the International Zeolite Association, and received numerous awards, including the P. H. Emmett award in Fundamental Catalysis of the ACS (1981), the Donald W. Breck award of the International Zeolite Association (1998), and the Blechner award (2001). He teaches organic chemistry, chemistry of natural products, chromatography, and heterogeneous catalysis.

The present review focuses on reactions catalyzed by transition metal complexes, immobilized on zeolites or ordered mesoporous molecular sieves. The focus is on fine chemicals reactions in the liquid phase. Reactions with transition metals incorporated in the framework of the molecular sieves are discussed in a separate paper in this issue;[6] the same holds for molecular sieves modified merely with organic groups, and for functionalized amorphous, nonordered SiO_2 supports.[6] Acid- or base-catalyzed reactions, and reactions with preformed metallic particles, e.g., hydrogenations, are outside the scope of this paper. Particular attention points are the effects of constrained matrices on the activity of immobilized metal complexes, the immobilization strategy, and the true heterogeneity of the observed catalysis. Moreover, it is our explicit aim to juxtapose early work with zeolite supports and more recent approaches using mesoporous molecular sieves. There are excellent previous reviews on this topic, for instance, by Venuto, Hölderich, and Jacobs for zeolite reactions,[7] or by Brunel, Corma, and Ying for the mesoporous molecular sieves;[8] however, comparison with the state-of-the-art at the end of 2001 shows that the field has rapidly expanded over the past few years.

II. Oxidation Reactions

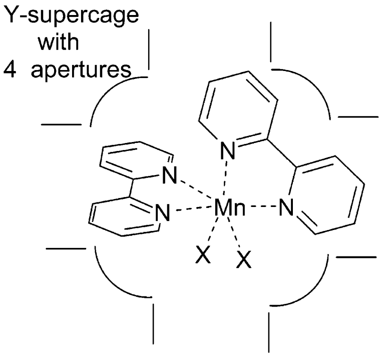
A. Olefin Oxidation

1. With H_2O_2

Framework substituted zeolites and mesoporous molecular sieves containing Ti have been very successful as catalysts for epoxidation with H_2O_2, as discussed in another paper in this issue.[6a] In the search for higher turnover frequencies, more accessible pore structures and better epoxide product stability, many alternative approaches have been explored. The major hurdle for many first-row metal catalysts, however, is excessive, unproductive decomposition of H_2O_2 to H_2O and O_2.[9]

The latter problem of aselective peroxide decomposition may in some cases be solved by immobilization of the complexes.[10] A beautiful example is the case of $Mn(bpy)_2^{n+}$ complexes (bpy = 2,2′-bipyridine). In solution, these compounds have a strong tendency to dimerize, and H_2O_2 is readily decomposed by these complexes via Mn−O−O−Mn intermediates. As a result, hardly any epoxidation is observed with homogeneous $Mn(bpy)_2^{2+}$; even with a 3-fold H_2O_2 excess with respect to cyclohexene, the epoxide yield on olefin basis remains below 1%. When these complexes are synthesized in faujasite supercages by adsorption of bipyridine on a Mn-exchanged zeolite, each zeolite cage can only contain one mononuclear $Mn(bpy)_2^{2+}$ complex (Scheme 1). Such mononuclear complexes less strongly decompose H_2O_2, and instead effect epoxidation, for instance, of cyclohexene.[10a] Again with a 3-fold excess of H_2O_2 to olefin, the eventual cyclohexane epoxide yield amounts to 41%. The zeolite additionally influences the product outcome by providing more or less acid sites around the epoxidation active site. Thus, in a NaX, there are hardly any acid sites, and high 1,2-epoxycyclohexane selectivities can be obtained. By contrast, in NaY, the zeolite acidity promotes epoxide opening to the trans diol, and the latter is further oxidized to hydroxyketones, diketones, or even acids. The same $Mn(bpy)_2^{2+}$ has also been successfully immobilized in siliceous or Al-containing MCM-41, and in MCM-48. In all these cases, beneficial effects of the immobilization on the catalytic epoxidation have been found.[10]

Scheme 1



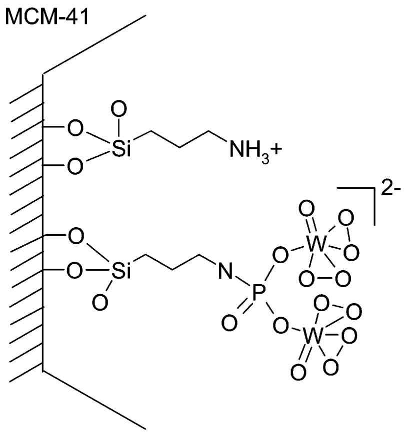
Prevention of H_2O_2 decomposition is also a major issue with the complexes of Mn^{n+} with the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane.[11] This complex is a useful epoxidation catalyst, if a way is found to suppress the catalase-like activity of the dinuclear complexes. When these compounds are synthesized inside faujasite zeolites, dimeric complexes are formed inside the relatively spacious supercages of the faujasite structure.[12a] With such a catalyst, epoxidation is only possible if acetone is used as a solvent. Particularly at low temperature, the latter forms perhemiketals with the peroxide, which is thus protected against fast decomposition. By contrast, truly mononuclear compounds are obtained if the triazacyclononane core is tethered to a silica support via a covalent link.[12b,c] For instance, the surface of SiO_2 or MCM-41 can be functionalized with glycidyl groups; these react with a dimethylated triazacyclononane to form an immobilized cheland that can bind Mn^{2+}. This way, mononuclear active sites are obtained, which are epoxidation catalysts in any solvent. A side effect of this immobilization is that apart from the epoxides, a small fraction of *cis*-diols are also formed. It has been demonstrated that the diols do not arise from epoxide hydrolysis, but that they are formed by a one-step incorporation of two oxygen atoms in the olefin. While the diol selectivities of 35% or less are not yet high enough to be of commercial relevance, such Mn dihydroxylation catalysts may on the long-term offer an alternative for more expensive Ru and Os catalysts.

While there is a prolific literature on homogeneous epoxidation catalysis with peroxides and W or Mo compounds, there are much less reports on heterogeneous catalysis with these elements. The reason is that Mo and W tend to form neutral or anionic complexes in contact with aqueous H_2O_2 or other peroxides; these are poorly or not at all withheld by siliceous or zeolite supports.[13] Hence other mechanisms must be provided for the retention of the catalytic elements on the support. For W-catalyzed epoxidation with H_2O_2, one may exploit the tendency of peroxo-W compounds to form stable associations with phosphorus(V) compounds. Thus a phosphoramide moiety has been tethered to the inner surface of MCM-41; the -NH-PO_3H_2 group binds W-peroxo compounds with formation of P−O−W bonds (Scheme 2).[14a] The heterogeneous nature of the resulting catalysts has been clearly proven.

Alternatively, deposition of phosphate species on a TS-1 zeolite provides docking points for anchoring of W oxoperoxo species.[14b] Indium has been incorporated in Beta zeolites as InO^+, and has been used as a catalyst in the epoxidation of cinnamyl alcohol with H_2O_2.[15]

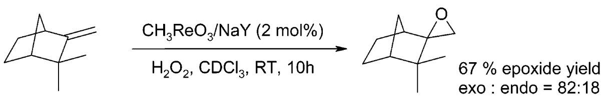
Finally, there are a few reports on zeolite-heterogenized versions of CH_3ReO_3.[16] This compound is an excellent catalyst for epoxidation with H_2O_2 but suffers from inconvenients such as acid-catalyzed epoxide opening or decomposition of the alkyl-Re

Scheme 2



bond to form perrhenates. Adam and co-workers have proposed reactions in CH_2Cl_2, with 3 vol % of concentrated H_2O_2 and 4 wt % of hydrated zeolite NaY.[16c] In these conditions, the polar H_2O_2 layer behaves like a liquid film, supported on the zeolite adsorbent. These reaction conditions were applied to the epoxidation of a series of olefins, and to the oxidation of silanes to silanols (Scheme 3):

Scheme 3



As a cheaper alternative, inorganic Re compounds such as Re_2O_7 and ReO_4^- have been deposited on oxides with Si−Al−O composition, including zeolites. With these catalysts, more drastic reaction conditions are needed than with CH_3ReO_3, e.g., reflux temperature, and use of anhydrous H_2O_2 in an organic solvent.[16a] The retention of the Re improves with increasing Al content of the support, pure Al_2O_3 being a more efficient support than zeolite Y.

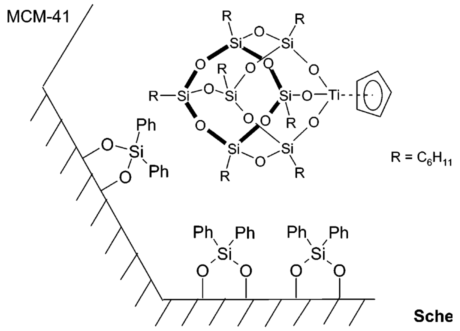
2. With Alkyl Hydroperoxides

Alkyl hydroperoxides are used on a large scale in industrial epoxidation, for instance, with tert-BuOOH and the heterogeneous "Shell" catalyst, which consists of Ti oxides anchored on a SiO_2 support. Obviously, selective epoxidation is only possible when the peroxide is activated on a metal that is not susceptible to one-electron redox processes. With many of the first row metals such as Fe, Cu, or Mn, such one-electron processes lead to aselective peroxide decomposition and radical reactions. For instance, with a Mn-exchanged NaY zeolite catalyst, oxidation of cyclohexene gives the allylic product di(2-cyclohexenyl) ether in 98% yield.[17] With an aromatic olefin such as styrene, allylic oxidation is of course impossible, and in such cases even radical reactions may result in epoxide formation. For instance, with a 14-fold excess of tBuOOH, *trans*-stilbene is transformed to its epoxide in up to 93% yield using different Mn-containing molecular sieves.[18] However, the reaction gives some epoxide selectively even without a catalyst. In the epoxidation of styrene with tBuOOH over Cu−Y zeolite or a Y zeolite containing copper phthalocyanines, epoxide selectivities remain below 40%.[19]

More selective epoxidation catalysts were obtained starting from metals such as Ti or Ru. In the preparation of Ti on SiO_2 catalysts, the last step is usually a calcination which removes any organic Ti ligands; this approach was also followed for Ti-MCM-41 catalysts prepared starting from titanocene compounds.[20] However, in some cases the material is even a useful epoxidation catalyst when the Ti precursor is left intact.[21] Van Santen et al. impregnated various MCM-41 precursors with a hexane solution of the silsesquioxane $[(c\text{-}C_6H_{11})_7Si_7O_{12}]\text{-Ti-}(\eta^5\text{-}C_5H_5)$. Such Ti-silsesquioxanes are relatively simple models for the active Ti sites in heterogeneous epoxidation catalysts; a catalyst concentration of 1 mol % of Ti is sufficient to convert even an unreactive olefin such as 1-octene for 80%, with an 80% epoxide selectivity.

In the case of heterogenized Ti-silsesquioxanes, the chemical composition of the mesoporous host has a clear influence on the retention of the Ti compound within the mesopores. If an Al-containing support is used, the Ti compound is leached out during the epoxidation of cyclooctene with tBuOOH. By contrast, true heterogeneity is observed for the Ti compound in a purely siliceous matrix, or alternatively, the catalyst retention can be improved by modification after Ti impregnation with $SiPh_2Cl_2$. The hydrophobic interactions between the peripheral cyclohexyl groups of the silsesquioxane and the apolar matrix seem sufficient to keep the Ti complex associated to the host (Scheme 4). Obviously, in the absence of a firm, permanent bond between the Ti compound and the support, one must always consider the risk of complex leaching.

Scheme 4

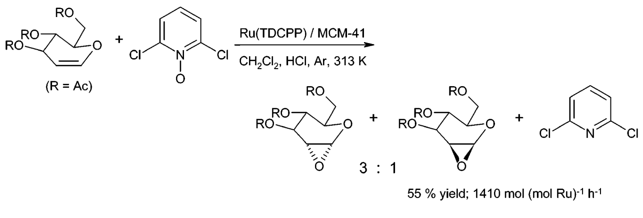


Some Ru catalysts can also be quite successful in two-electron redox processes with tBuOOH. Planar Ru-porphyrins can be immobilized on aminopropyl groups that are covalently grafted to the mesopores of MCM-41.[22] With Ru(II) *meso*-tetrakis(4-chlorophenyl)porphyrin, $[Ru^{II}(TCPP)(CO)(EtOH)]$ as the precursor, the anchored amine ligand displaces an axial EtOH ligand and this coordinative binding is sufficient for retention of the complex in catalytic conditions. In comparison with the homogeneous complex, the immobilized porphyrin is more resistant to oxidative degradation, with total turnover numbers up to 50 times higher. For instance, in the epoxidation of norbornene, 9000 turnovers were achieved with the immobilized catalyst over 30 h, while the homogeneous complex was deactivated after 6 h and 230 turnovers. This beneficial effect of immobilization is clearly due to site isolation of the porphyrins. However, epoxide selectivities in these reactions with tBuOOH were only moderate: with cyclohexene, the allylic alcohol (33%) and ketone (57%) were the main products; with styrene, benzaldehyde was produced (70%).

3. With Amine Oxides

A very similar catalyst, based on a porphyrin with 2,6-dichlorophenyl meso substituents, was used by Che and co-workers in epoxidations with 2,6-dichloropyridine *N*-oxide as the terminal oxidant.[23] This oxidant converts the Ru to a Ru(V)oxo species or a Ru(IV)oxo porphyrin radical. Regeneration of the remaining pyridine with an oxidant such as H_2O_2 is straightforward. The steric constraints exerted by the MCM pores and the bulky porphyrin result in unusual stereo- and regioselectivities. For instance, in limonene, the disubstituted exocyclic double bond is preferred over the endocyclic trisubstituted bond; based on electronic effects, the more substituted bond should be epoxidized first. Another remarkable reaction is the epoxidation of 3,4,6-tri-*O*-acetyl-D-glucal. Even if the reaction requires 30 mol % of HCl, the notoriously labile glycal epoxides are formed in high yield in the anhydrous reaction medium (Scheme 5).

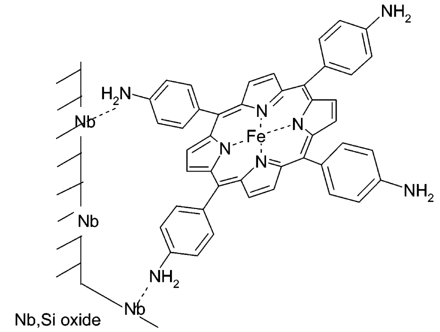
Scheme 5



4. With PhIO

While iodosylbenzene is an expensive and dirty oxidant, it has often been used in reactivity studies particularly with porphyrin and phthalocyanine catalysts. However, even then careful tuning of the redox properties of the metallomacrocycle remains necessary to favor the epoxidation reaction.[24] For instance, with an Fe-cyclam type complex entrapped in a Y zeolite, allylic oxidation was the major pathway in cyclohexene oxidation with PhIO.[25] In other cases, the epoxidizing properties of the homogeneous catalysts were successfully preserved after the heterogenization, for instance, with Fe-porphyrins encapsulated in zeolite X, or with pentadentate Mn−Schiff base complexes covalently anchored to MCM-41.[8a,26] In an original approach, MCM-41 materials were used in which between 5 and 20% of the Si is replaced by Nb.[27] This Lewis-acid Nb can act as a docking point for amino groups attached to the periphery of the porphyrin, as in Fe^{III}-tetrakis-4-aminophenylporphyrin-Br (Scheme 6). Particularly the material with 5% Nb, which has a pore diameter of 3.3 nm, is a fast and selective epoxidation catalyst even with cyclohexene. The peripheral attachment and the large pore size probably result in a minimal perturbation of the porphyrin geometry, while the porosity also ensures facile reagent and product transport.

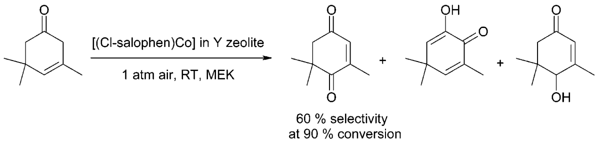
Scheme 6



5. With O_2

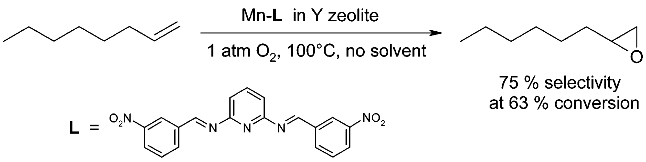
Direct olefin epoxidation using both atoms of dioxygen remains a formidable and unsolved challenge for liquid-phase catalysis, perhaps with the exception of some Ru(VI)-*trans*-dioxo porphyrin catalysts. Often the reaction leads to allylic oxidation instead of epoxidation. However, these reactions can be quite synthetically useful. For instance, the allylic autoxidation of β-isophorone leads to keto-isophorone in high yields using zeolites in which Co is chelated by various Schiff base ligands formed from *o*-phenylenediimine and substituted salicylaldehydes.[28] Keto-isophorone is a precursor to some compounds of the vitamin A and E series. At a conversion of 90%, a 60% selectivity for the keto-isophorone was obtained (Scheme 7). The catalytic activity is particularly high when electron-withdrawing substituents are present on the Schiff base; this electronic fine-tuning probably gives Co^{II}/Co^{III} the right redox potential to intervene in the one-electron redox processes of the autoxidation.

Scheme 7



In other cases, a co-reductant is needed to direct the reaction toward epoxidation. In the well-known Mukayiama reaction, a sacrificial aldehyde is used, which is autoxidized to the acid; the peracid intermediate effects the epoxidation, possibly with intervention of a metal catalyst. Many heterogenized metal catalysts can assist the initial autoxidation of the aldehyde to the peracid, for instance, Mn or Co substituted in aluminophosphates, Co chelated by covalently anchored carboxylic acids, or the heteropoly compound $H_5PV_2Mo_{10}O_{40}$ on amino-modified MCM-41.[29] In one recent intriguing report, the catalyst is a zeolite-Y entrapped complex of Mn with a Schiff base.[30] Pure 1-octene is reacted with 1 wt % of the catalyst in the absence of a co-reductant or a solvent at 373 K. At a 1-octene conversion of 63%, epoxide selectivity is 75%, which amounts to a 47% yield (Scheme 8):

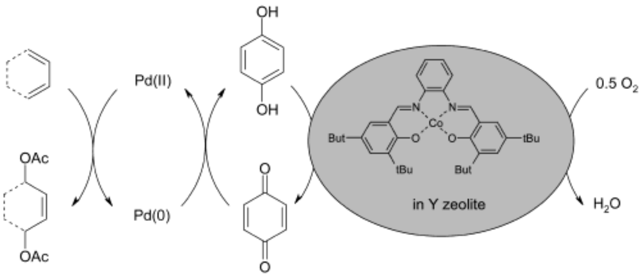
Scheme 8



The gradually increasing reaction rate and the clear induction time at lower temperatures show that the process is of a radical type, with the Mn catalyst accelerating one-electron reactions. The fact that 1-octene has only two H atoms in the allylic position certainly favors epoxidation over allylic H abstraction. While side products were not identified, it seems likely that a fraction of the 1-octene is oxidized to smaller fragments; during the deeper oxidation of one molecule of 1-octene, several peracids or acylperoxy radicals are formed, which can epoxidize up to three other molecules of 1-octene.

Diacetoxylation of 1,3-dienes is a Pd-mediated reaction, in which the Pd is reduced to the zerovalent state after elimination of the diacetoxylated product. For instance, 1,3-cyclohexadiene is converted to 1,4-diacetoxy-2-cyclohexene. To reoxidize the Pd(0) to its initial divalent state, a redox chain has been proposed, in which the electrons are shuttled from Pd(0) to *para*-quinone, and hence to a Co-macrocycle which activates dioxygen (Scheme 9).[31] However, the latter compounds are prone to deactivation by dimerization and degradation. Much more stable catalysts are obtained by using zeolite entrapped Co Schiff bases, such as Co-tetrabutyl-salophen.[31] In combination with $Pd(OAc)_2$ and hydroquinone and in acetic acid as the solvent, 7 mol of diene are acetoxylated per mole of Pd in one hour.

Scheme 9



Similar electron-transfer chains can be used in the oxidation of hydroquinone, in the Pd-catalyzed Wacker oxidation of 1-octene to 2-octanone, or in the Ru-catalyzed oxidation of benzyl alcohol. Note that for the Pd and Ru reactions, the actual catalyst is not heterogeneous; only one of the cocatalysts is effectively immobilized. Alternative zeolite-based Wacker Pd catalysts have been proposed for gas-phase olefin ketonization.[32] For instance, $Pd(NH_3)_4^{2+}$ and Cu^{2+} can be co-exchanged on a Y zeolite, and such materials catalyze the oxidation of propene to acetone with O_2.

B. Oxidation of Aliphatic Hydrocarbons

There are numerous reports on catalytic alkane oxidation using heterogeneous catalysts and single-oxygen atom donors such as tBuOOH or H_2O_2 as the oxidant. Exemplary catalysts based on molecular sieves are:

(i) metallophthalocyanines and metalloporphyrins synthesized in the inner pore volume of zeolites (M = Cu, Fe, Co, ...) or mesoporous sieves,[33−35]

(ii) zeolite-entrapped metallophthalocyanines, embedded in polymeric membranes,[36]

(iii) cationic Fe-porphyrins around which zeolite X is synthesized, or exchanged on the outer surface of zeolites,[26a,37]

(iv) cationic polyamine or polyimine complexes of Mn, Fe, ... entrapped in zeolites,[38]

(v) Fe- or V-picolinate complexes encapsulated in zeolites such as Y and mordenite,[39]

(vi) cations coordinated on covalently anchored groups, e.g., amino groups in MCM-41, etc.[40,41]

Alkane oxidation reactions may be initiated by the homolytic decomposition of ROOH by the catalyst via the Haber Weiss cycle (R = H, alkyl, or acyl). Any metal that easily switches between two redox states (n^+) and ($(n+1)^+$) may be a suitable catalyst for the reaction 1:

$$\text{(A) } 2\,\mathrm{ROOH} \rightarrow \mathrm{RO}^{\circ} + \mathrm{ROO}^{\circ} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{RO}^{\circ} + \mathrm{R'H} \rightarrow \mathrm{R'}^{\circ} + \mathrm{ROH} \qquad (2)$$

$$\mathrm{R'}^{\circ} + \mathrm{O_2} \rightarrow \mathrm{R'OO}^{\circ} \qquad (3)$$

$$\mathrm{R'OO}^{\circ} + \mathrm{R'H} \rightarrow \mathrm{R'OOH} + \mathrm{R'}^{\circ} \qquad (4)$$

$$2\,\mathrm{R'OO}^{\circ} \rightarrow \text{alcohol} + \text{ketone} + \mathrm{O_2} \qquad (5)$$

Reaction of the formed free radicals with the alkane substrate (R′H) leads to oxygenation. If this route is the only mechanism, hydroperoxides are among the primary products; for a secondary alkane substrate, both ketone and alcohol are produced in a 1:1 ratio. Alternatively, for Fe and Mn catalysts, an additional pathway (B) with two-electron redox chemistry may be available if a proper ligand is positioned around the metal ion. Porphyrins (por) and phthalocyanines are the best-studied chelands in this chemistry. Typically, the peroxide oxidizes the M^{n+} center, e.g., Fe^{3+}, to a $M^{n+2}{=}O$ moiety, e.g., an $Fe^{V}{=}O$ oxo complex, or in the case of porphyrins, an $Fe^{IV}{=}O$ porphyrin cation radical. This oxo complex abstracts a H° radical from R′H to form a metal-bound OH group; after very fast recombination with R'°, an alcohol product is formed:

$$\text{(B) } \mathrm{Fe^{III}(por)} + \mathrm{ROOH} \rightarrow \mathrm{Fe^{V}{=}O(por)} + \mathrm{ROH} \qquad (6)$$

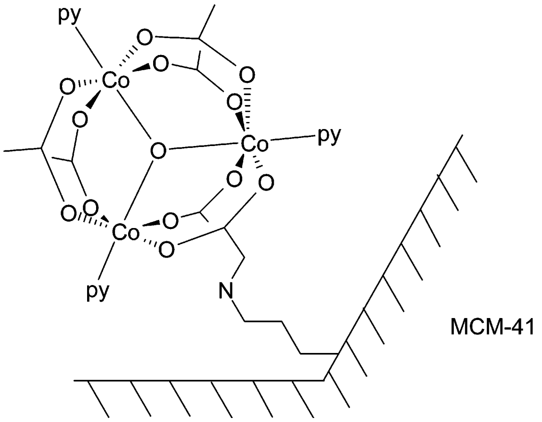
$$\mathrm{Fe^{V}{=}O(por)} + \mathrm{R'H} \rightarrow \mathrm{Fe^{IV}{-}OH(por)} + \mathrm{R'}^{\circ} \qquad (7)$$

$$\mathrm{Fe^{IV}{-}OH(por)} + \mathrm{R'}^{\circ} \rightarrow \mathrm{Fe^{III}(por)} + \mathrm{ROH} \qquad (8)$$

In many cases, the two-electron pathway with peroxide heterolysis (B) seems to prevail based on experimental observations such as high alcohol selectivity, or high yields on peroxide basis. High kinetic isotope (KIE) effects may be an additional piece of evidence for the “oxygen-rebound” mechanism of route (B), since radical reactions usually have a k_H/k_D of almost one.[36]

Which process predominates depends on many factors, such as the metal, the ligand, the oxidant, the supporting matrix, and the substrate. For instance, with a bulky tertiary hydrocarbon substrate such as pinane, a zeolite-entrapped Fe-phthalocyanine catalyst and tBuOOH, step (7) is sterically hindered, and route (A) predominates, with 80% hydroperoxide selectivity at 90% hydrocarbon conversion.[42] *Free* radical reactions also occur when simple Mn^{n+}- or Fe^{n+}-exchanged zeolites are used with tBuOOH in the oxidation of cyclohexane or cyclic aliphatic ethers.[38b,c] Even when ligands are added to modify the redox potential of the zeolite-exchanged cation, the reactions may still proceed via homolytic pathways.[38] One-electron processes occur as well with the trinuclear acetate-bridged Co-catalyst, immobilized in MCM-41 channels on covalently anchored glycine moieties (Scheme 10).[41]

Scheme 10



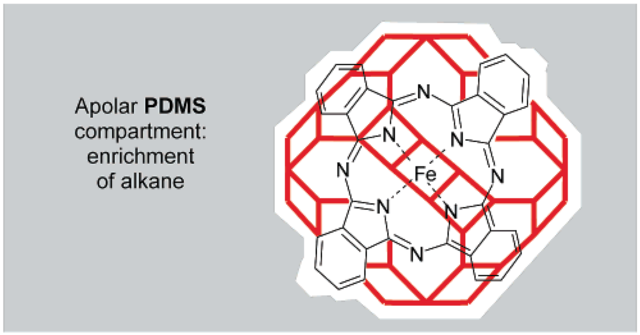
The molecular design of this catalyst is inspired on the active species in industrial free radical autoxidation. In conditions that resemble those of the much-debated Gif chemistry, viz. in acetonitrile/pyridine,[43] zeolite-entrapped Fe-picolinate complexes likely use radical mechanisms in the oxidation of cycloalkanes with H_2O_2.[44] With the latter two catalysts, very high ketone selectivities of 80 up to 90% can be achieved.

In contrast, when the oxidant is PhIO, use of an immobilized porphyrin catalyst leads to >90% alcohol selectivity, which is clear proof for route (B).[26a] Secondary alkane oxidation with tBuOOH as oxidant is clearly also a heterolytic process with Fe-phthalocyanines, synthesized in situ in the cages of zeolite Y, as proven by the high KIE.[36] With the latter catalyst, a proper synthesis procedure is important: if an ion-exchanged Fe^{3+}-zeolite is used as a precursor, a lot of Fe^{3+} remains unchelated on the zeolite after formation of the phthalocyanines. This free Fe^{3+} catalyzes the Haber-Weiss decomposition of the peroxides (reaction 1), which results in very low yields on peroxide basis. However, when ferrocene is used as an Fe source, almost all Fe^{3+} is chelated in the phthalocyanines, and oxygenation yields are much improved.[34]

The nature of the support has several important effects on these reactions. First, the site isolation of the reaction centers over the matrix impedes that one catalytic center is oxidatively destroyed by another one. Consequently, the catalyst lifetime, expressed as total turnover number, is usually much higher for the immobilized than for the dissolved complex. This has been amply demonstrated in the case of zeolite-entrapped phthalocyanine catalysts.[33-36] While a homogeneous Fe-phthalocyanine (FePc) in contact with tBuOOH is fully deactivated after 10 turnovers or less, the zeolite-immobilized phthalocyanines easily attain turnover numbers of 200.

Second, the polarity of the matrix has an important effect on the concentration of the reagents close to the active site. In a polar matrix, e.g., a Y zeolite with Si:Al = 2.5, adsorption of a polar oxidant such as tBuOOH is highly favored over alkane sorption, and this promotes undesired peroxide disproportionation. Thus, for cyclohexane oxidation with tBuOOH catalyzed by FePc in zeolite Y, oxygenate yields on peroxide basis are usually below 40%. This figure can be substantially increased, up to 60%, by using a less polar, ultrastabilized Y zeolite as a support. Alternatively, zeolite-entrapped FePc complexes were embedded in a hydrophobic, elastomeric poly(dimethylsiloxane) matrix (Scheme 11).[36] This design is reminiscent of the location of cytochrome P-450 in natural systems: due to its location in lipid membranes, the enzyme gains activity or stability. Similarly, the membrane-entrapped catalyst displays higher activity, and is more resistant toward poisoning by excessive adsorption of polar reagents or reaction products. With the membrane-embedded FePcY, total turnover numbers attain 1000 within 5 h.

Scheme 11



The interaction between matrix and complex also has a decisive influence on the true heterogeneity of the catalyst, and the possible contribution by leached, homogeneous species. Excellent heterogeneity is displayed by zeolite-entrapped phthalocyanines, partly because the nonionic phthalocyanines are poorly soluble in many solvents. Exchange of cationic porphyrins or phthalocyanines also guarantees complex retention on ion exchangers such as zeolites. By contrast, leaching has been reported for metal ions coordinated on aminopropylated MCM,[40] and for small, neutral encapsulated complexes such as V-picolinates in zeolites.[39]

Particularly interesting possibilities are offered by fine-tuning of the electronic properties of the heterogenized complexes. Thus, turnover numbers can be strongly increased in alkane oxidation with tBuOOH by introduction of electron-withdrawing NO_2-groups in zeolite-entrapped FePc.[34b] In otherwise similar conditions, turnover numbers after 30 h in cyclohexane oxidation with tBuOOH amount to 4000 for nitrosubstituted zeolite-entrapped phthalocyanines, versus 400 for the nonsubstituted complexes. Even more special effects have been observed with encapsulated polychlorinated phthalocyanines.[33] Raja and Ratnasamy report that even with O_2 as the oxidant, oxidation of *n*-hexane over NaY entrapped $CuCl_{14}Pc$ leads to oxidation of the primary carbon atoms, with hardly any secondary oxidation. Thus, at 333 K and 7 bar air pressure, and with 10 wt % catalyst, the only products from neat *n*-hexane are 1-hexanol and hexanal, in yields of 2.8 and 6.1% respectively. This interesting lead observation deserves further follow-up.

C. Oxidation of Aromatic Compounds

1. Ring Hydroxylation of Aromatic Compounds

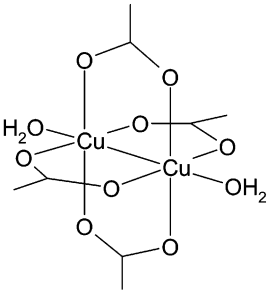
In analogy to the classical Fenton hydroxylation of aromatic rings using Fe^{II}/Fe^{III} and H_2O_2, many heterogeneous variants have been proposed based on zeolites or related molecular sieves. Exemplary catalysts are Fe^{III}-exchanged ZSM-5, FePc deposited on zeolite A, MCM-41 with deposited Fe^{III}(acetylacetonate)$_3$ or Fe^{II}(8-quinolinol)$_3$, Fe^{III} on MCM-48, or Cu in zeolites or mesoporous molecular sieves, possibly assisted by UV light.[45] Catechol and hydroquinone are typically produced in a 2:1 ratio; water is often the preferred solvent. Depending on parameters such as the pH and the ion exchange capacity of the support, several of these catalysts are probably truly heterogeneous. Higher pH and higher exchange capacity are expected to result in better metal retention, particularly for simple aquo-anions. A somewhat different reaction is obtained by oxidation of phenol with H_2O_2 using zeolite-supported Cu-phthalocyanines with electron-withdrawing groups, such as Cu(NO_2)$_4$Pc or $CuCl_{14}Pc$.[33,46] With the polychlorinated Pc, a total Cu turnover number of 8 is obtained, versus 4 turnovers with the nitrosubstituted Pc. However, with the latter, a surprisingly high 100% selectivity for para-hydroxylation is observed in acetonitrile as the solvent.

A nice example of fine chemicals preparation comes from work with supported Fe-tetrasulfophthalocyanines on amino-modified MCM-41. The dimeric Fe−O−Fe form of the phthalocyanines appeared an active catalyst for tBuOOH oxidation of 2-methylnaphthalene to vitamin K_3 (2-methylnaphthoquinone) and of 2,3,6-trimethylphenol to trimethylbenzoquinone.[47]

Particular catalytic properties have been attributed to Cu acetate dimers in zeolites such as Y, MCM-22, in the aluminophosphate VPI-5 or in the cubic mesoporous molecular sieve MCM-48 (Scheme 12).[48,49] By contrast with all previous systems, these materials are successful catalysts in reactions with O_2 as the oxidant.

As the catalytic activity in aerial oxidation seems linked to dimeric, tetraacetato bridged complexes rather than to monomeric exchanged Cu^{II} ions on zeolite lattice sites, conditions that lead to Cu^{II} exchanged on lattice oxygen atoms are avoided. Thus, the zeolites are loaded with Cu in concentrated, 0.45 M solutions of Cu acetate monohydrate, which contains already the dimeric compound. Remarkably, despite the Cu excess offered, the zeolites contain only ~0.1 wt. % Cu, which is 100 times below the cation exchange capacity of the Y zeolite (Si/Al = 2.5). In some cases, additional exposure to (chloro)acetic acid vapors was required to obtain catalytically active solids. Convincing proof for dimer formation in the zeolite comes from EPR.[49] The dimers display a spectrum that is quite different from the $S = 1/2$ spectra of exchanged Cu^{2+}. In the dimer, the two spins are coupled antiferromagnetically at very low temperature ($S = 0$), but at 86 or 298 K the $S = 1$ triplet state is partly populated, giving rise to ESR spectra with a 7-line hyperfine structure due to the two Cu^{II} nuclei. While part of the Cu^{II} is present in the dimers, part of the Cu also simply occupies exchange sites.

Scheme 12



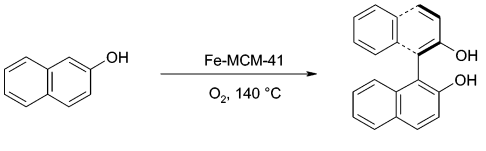
The activity of these entrapped Cu acetate dimers has been evaluated in the aerial oxidation of phenols, which is in nature catalyzed by the dicopper enzyme tyrosinase.[48,49] At 298 K and at pH = 6.5, orthoquinones are formed from phenol and *o*- or *m*-cresol. Starting from L-tyrosine, the orthohydroxylated product L-DOPA is obtained, particularly in the presence of ascorbic acid, which may reduce the primary quinone product. The entrapped complexes display a much higher catalytic activity than Cu acetate monohydrate as such. For instance, in the aerial phenol hydroxylation, the total turnover number, i.e., moles of product per mole of Cu, amounts to 4 in the case of copper acetate, versus 36 in the case of copper dimers in MCM-22. This may be ascribed to changed electronic properties of the complexes, as inferred from the zero-field splitting parameters, or to a higher dispersion of the encapsulated Cu acetate, since the neat monohydrate is only poorly soluble in the reaction conditions, viz. an aqueous phosphate buffer at pH 6.5. However, some aspects of this remarkable biomimetic catalyst deserve further elucidation. Thus, Cu^{II} ions are leached from the zeolite above room temperature or at acid pH (<4.0); this raises the issue whether acidity on the zeolite itself influences the catalyst stability. Moreover, a tentative mechanism has been proposed, in which two phenolates coordinate to the Cu^{II} dimer and reduce it to a Cu^I dimer, which binds O_2 in a Cu_2−O_2 site. Subsequent oxygen transfer to the aromatic rings and release of orthoquinone brings the catalyst back in the deoxygenated state. However, this proposal requires further proof.

Related work has been reported for the oxidation of benzene to phenol with O_2 over Cu-containing catalysts. However, phenol yields are very low (<1%), and 20 mol % of ascorbic acid are needed as a co-reductant.[50]

2. Oxidative coupling of aromatics

An alternative reaction is the oxidative coupling of two aromatic rings to form biaryls. Various zeolite- or MCM-41-based catalysts have been used as catalysts in these reactions. For instance, in the coupling of 2,6-di-*tert*-butylphenol to the corresponding diphenoquinone, CoX may be used as a catalyst with tBuOOH as an oxidant or initiator of the radical reaction.[51] Alternatively, O_2 may be used as an oxidant, with Cu-exchanged or Cu-impregnated MCM-41 as the catalyst.[52] In this case, addition of base not only promotes the formation of phenolate anions and thus initiates the reaction; the base also confines the Cu to the support by formation of insoluble Cu-hydroxide particles. An appealing related example is the oxidative coupling of 2-naphthol to the important ligand precursor 1,1′-bi-2-naphthol with O_2 as the oxidant.[53] The reaction proceeds more easily over Fe^{3+}-exchanged MCM-41 than over an Fe^{3+}-exchanged zeolite, due to the large size of the binaphthol product, which is too large to leave the faujasite structure through the 12-MR windows (Scheme 13):[53a]

Scheme 13



The reaction is truly heterogeneous as proven by a filtrate test, but a catalyst mass three times larger than the product mass was employed.

3. Side Chain Oxidation of Alkylaromatics

Oxidation of *p*-xylene to terephthalic acid is a large scale operation in industry. A homogeneous catalyst is used, consisting of a mixture of $Co^{II/III}$ and $Mn^{II/III}$ with Br^- as a promoter. A zeolite-based heterogeneous form of this catalyst was recently proposed.[54] In the preparation, zeolite Y is exchanged with Co^{II} and Mn^{II} in a 1 to 2 ratio, followed by exposure to a mixture of pyridine, NaBr, and H_2O_2 in acetic acid. As a structure for the species inside the zeolite, the trinuclear μ_3-oxo-bridged cluster $[CoMn_2(\mu_3{-}O)(MeCO_2)_6(pyr)_3]$ was proposed. However, the EPR spectra shown do not allow one to clearly distinguish the trinuclear cluster from simple Mn(II) ions, coordinated to the zeolite lattice, and a variety of species may well coexist in the zeolite cavities. Most importantly, the material appears to be an excellent catalyst for the autoxidation of 5 vol % *p*-xylene in acetic acid at 473 K. At 100% xylene conversion, the diacid selectivity is 99.4%, and analysis reveals only traces of 4-carboxybenzaldehyde. The latter product is rather resistant to further oxidation. While no detailed data on the number of effective catalyst recycles are given, one may question the long-term stability of the zeolites in aqueous acid.[54] For autoxidation of ethylbenzene to acetophenone, a Cr^{3+} catalyst bound to a mesoporous SiO_2 via a covalently linked Schiff base was employed;[55a] the long-term stability of such imines in autoxidation conditions at 413 K deserves closer attention. Ethylbenzene side chain oxidation has also been performed with a series of zeolite-embedded transition metal complexes of 3-formylsalicylic acid, in combination with H_2O_2 as oxidant.[55b]

D. Alcohol Oxidation

Perruthenate has been immobilized on quaternary ammonium groups in the channels of MCM-41.[56] The material catalyzes the oxidation of primary alcohol groups to aldehydes in essentially quantitative yield. Typical substrates are geraniol, benzylic alcohols, and cinnamyl alcohol. Pure oxygen is the oxidant at 353 K, or alternatively amine oxides such as trimethylamine *N*-oxide are employed. The case is interesting since the same authors have compared their material to analogous catalysts. The MCM-based material has superior catalytic performance in comparison with a functionalized polystyrene, which seems due to oxidative degradation of the latter support. Moreover, in reactions with perruthenate on an amorphous aerogel, significantly longer reaction times were required than with the ordered mesoporous material, showing that increased loadings and better access to pores lead eventually to more performant catalysts.

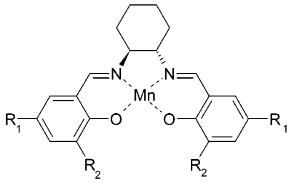
Benzyl alcohol has also been oxidized to benzaldehyde with tBuOOH using a μ-oxo bridged, dinuclear Fe-phenantroline complex supported on MCM-41.[57]

E. Enantioselective Oxidations of Olefins

Jacobsen's epoxidation catalyst, a chiral Mn Schiff base complex with bulky substituents, has been the subject of many heterogenization attempts.[58] Obviously, not only activity but also enantioselectivity should be preserved in the immobilized complex. Initial research has focused on attachment to polymer carriers.[59] However, in many cases interactions between the polymer backbone and the complex appeared to have a deleterious effect on the enantioselectivity, thus necessitating, e.g., the use of large spacers between complex and support. Such often impredictable interactions may be avoided by the use of well-organized microporous or mesoporous supports. There have been interesting developments both with MCM-41-type carriers and with zeolite hosts.

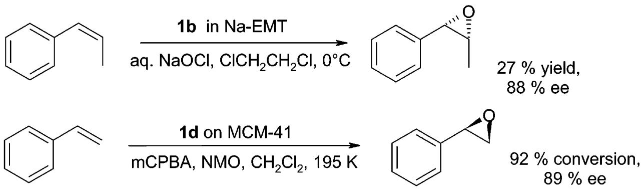
Zeolite-entrapped metal Schiff base complexes have been known for some time. Typically, the free Schiff base is adsorbed on a metal-exchanged zeolite; if the kinetic diameter of the chelate is larger than that of the ligand, truly entrapped complexes may be obtained. Alternatively, the Schiff base may be assembled from the diamine and the substituted salicylaldehyde inside a metal-exchanged zeolite.[60a,b] One of the first demonstrations that these materials could be useful catalysts was provided by Dutta, who used a Mn-salen loaded Y zeolite as a catalyst for the epoxidation of aromatic olefins with PhIO;[60c] recently, similar catalysts were used for epoxidation of α-pinene with O_2 and a sacrificial aldehyde reductant.[60d] Enantioselective reactions with zeolite-entrapped Mn Schiff bases have been approached in various ways. A particular difficulty is that the Jacobsen complex as such is too large to fit for instance in the supercage of a Y zeolite. Accordingly, the bulky *tert*-butyl groups were omitted for entrapment of the chiral complex **1a** in the supercages of zeolite Y; a complex with CH_3 substituents instead of tBu (**1b**) was synthesized in the slightly larger hypercage of hexagonal faujasite with EMT topology (Scheme 14).[61] Even if the molecular structure of these entrapped compounds differs from that of Jacobsen's original complex, excellent results have been obtained, for instance, in the epoxidation of cis-β-methylstyrene (Scheme 15):

Scheme 14



1a: $R_1 = R_2 = H$
1b: $R_1 =$ Me, $R_2 =$tBu
Jacobsen catalyst: $R_1 = R_2 =$ tBu

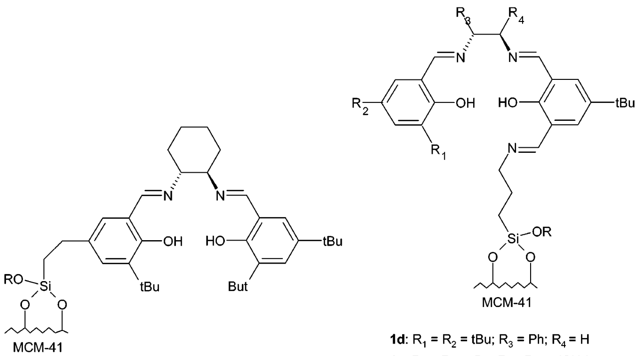
Scheme 15



This implies that not only the substituents on the Schiff base ligand, but also the zeolite cage imposes steric constraints on the interaction of the olefin reactant with the active Mn-oxo species. Alternatively, the space available for the bulky complex can be enlarged by $SiCl_4$ treatment or steaming, which create mesopores in the zeolite structure.[62] A very elegant approach was followed by Balkus et al.[63] They added Jacobsen's complex to the layered precursor of a zeolite with MWW topology. Subsequent heat treatment causes transformation of the layered precursor to MCM-22 zeolite crystals; the Jacobsen complex is easily accommodated in the very spacious supercages of this structure. The entrapped complex is not only more active than the homogeneous counterpart, with 145 turnovers/h versus 55 for the homogeneous Jacobsen catalyst; due to the entrapment in the zeolite cage, enhanced enantioselectivities are observed, e.g., 91% ee in the epoxidation of α-methylstyrene with bleach instead of 51% ee with the homogeneous catalyst in the same conditions.

When a MCM-41 type carrier is used, steric entrapment of the complex is not possible, and covalent linking seems the most reliable method for complex heterogenization, in analogy with some work using amorphous SiO_2 as a carrier.[64] A single attachment point on the ligand seems to induce less distortion in the complex than a double-sided attachment, and hence allows one to achieve better enantioselectivity.[65] For instance, complex **1c** was grafted on MCM-41 by reaction of a vinyl-substituted Schiff base on a hydride-functionalized surface (Scheme 16).[65a] With this complex, 75% ee was observed in the enantioselective epoxidation of 1-phenyl-1-cyclohexene, using PhIO in acetonitrile, at 22% conversion and 88% chemoselectivity for the epoxide. With **1c**, chemoselectivity, activity, and enantioselectivity remained unchanged over at least 4 cycles. Another remarkable catalyst was prepared by stepwise assembly of the Schiff bases **1d**, **1e**, and **1f** starting from an aminopropylated MCM-41.[65b] In the epoxidation of styrene with NMO at 195 K using **1f** ($R_1 = R_2 =$ H), 89% ee was obtained at 92% olefin conversion (Scheme 15). In contrast, with catalysts **1d** and **1e**, in which $R_1 = R_2 =$ tBu, slightly lower ee-values of 86 and 65%, respectively, are observed.

Scheme 16



1c

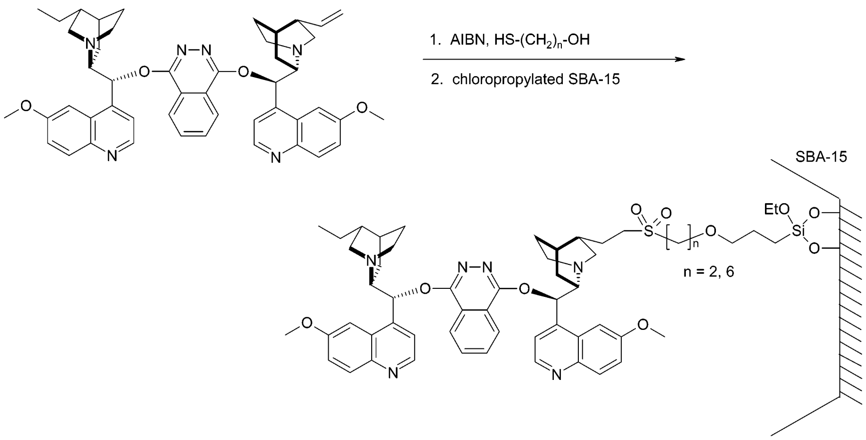
1d: $R_1 = R_2 =$ tBu; $R_3 =$ Ph; $R_4 =$ H
1e: $R_1 = R_2 =$ tBu; $R_3 - R_4 = -(CH_2)_4-$
1f: $R_1 = R_2 =$ H; $R_3 =$ Ph; $R_4 =$ H

Thus, equal or even superior enantioselectivity is obtained with structure **1f**, which contains small H substituents instead of the bulky tBu groups. This proves that the support to which the compounds are attached can play in role in directing the approach of the reacting molecules. In a recently reported covalent approach, a triazine-based linker was employed; enantioselectivities up to 84% were obtained.[65c]

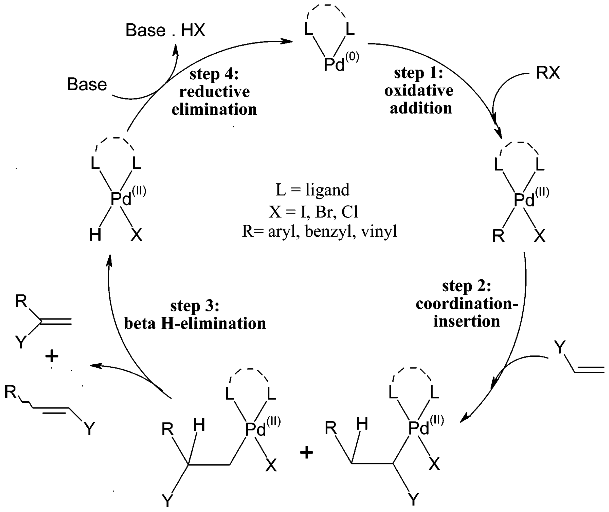
Finally, the Jacobsen complex can be immobilized in the pores of Al-containing MCM-41. Either the complex as a whole is introduced into the support, or the ligand is adsorbed on an ion-exchanged Mn-(Si,Al)-MCM-41.[66,67] In both cases, it is hoped that the small electrostatic interaction between the complex (with a charge +1) and the MCM-41 will be sufficient for retention of the catalyst within the pores. Varying results have been obtained in recycling the catalysts, for instance, Hutchings et al. observed a sharp decline of epoxide yield and ee in a second cycle with the catalyst.[67]

There are scattered recent reports on immobilization of Sharpless' chiral epoxidation catalyst.[68] Li and co-workers have anchored a tartrate ester on MCM-41 and amorphous SiO_2; after coordination of $Ti(OPr^i)_4$, the material catalyzes the enantioselective epoxidation of allyl alcohol with 80% ee.[68a] Typical turnover numbers on Ti basis are between 10 and 15. Strikingly, it is claimed that the active center on the heterogenized catalyst is a monomeric Ti species,

Scheme 17



Scheme 18



while there is ample evidence that in homogeneous catalysis, both monomeric and dimeric Ti species are involved.[68b,c] A heterogeneous catalyst with similar performance had previously been designed by anchoring of an organometallic Ta compound to a silica surface, and subsequent addition of diethyl tartrate.[68d]

Catalyst immobilization is as well a technological necessity for the Sharpless asymmetric dihydroxylation, in view of the cost of the Os and the chiral cinchona alkaloid ligand. For instance, a dimeric phthalazine ligand was coupled to chloropropylated SBA-15 using thioalcohol spacers of varying length (Scheme 17).[69] After addition of OsO_4, the heterogenized ligand was used in dihydroxylation of, e.g., ethylcinnamate, in a biphasic solvent system containing $K_3Fe(CN)_6$, K_2CO_3, tBuOH, and water. Ee's were comparable or even superior to those of the homogeneous catalyst. Upon reuse of the immobilized catalyst, very low activity is noticed, because almost all OsO_4 is lost in the washing procedure. However, addition of an extra Os dose restores the activity. For immobilization of the Os itself, other specific strategies would be needed.[70]

Finally, there are reports on immobilization of chiral Mo epoxidation catalysts by covalent attachment of ligands.[71,72] For instance, dioxoMo moieties were attached to a ligand derived from hydroxyproline, anchored in mesoporous US−Y zeolite; these catalysts were applied in the enantioselective and chemoselective β,γ-epoxidation of geraniol and nerol.[72]

III. C–C Bond Formation

A. Heck Reactions

The palladium catalyzed arylation and vinylation of olefins, known as the Heck reaction, is a tolerant and versatile method for C−C bond formation (Scheme 18).[73]

Nevertheless, only in a few industrial reactions, this chemistry is applied, for instance, in the synthesis of an intermediate of the sulfonylurea Polysulfuron and in the synthesis of the UV-absorber octylmethoxycinnamate.[74] Heck chemistry still faces some major problems, such as the activation of chloroaromatics in mild conditions, the production of salt waste, and the need for sometimes large amounts of Pd. Particularly the last aspect has elicited several attempts to use heterogeneous catalysts.[73b,73d,75−80] Whether these catalysts are truly heterogeneous depends not only on the molecular architecture of the Pd-support interaction, but also on the reaction conditions such as temperature, solvent, and base.

Zeolite supports including faujasite and mordenite have been functionalized with Pd via exchange with $Pd(NH_3)_4^{2+}$, or alternatively via impregnation with $Pd(OAc)_2$, $[Pd(C_3H_5)Cl]_2$, or the palladacyclic compound $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$.[76] Such catalysts are useful, e.g., in the Heck reaction of 4-bromofluorobenzene with styrene at 100 °C in dimethylacetamide (DMA) and with NaOAc as the base (Table 1). With $Pd(NH_3)_4^{2+}/Y$ as catalyst, it is even possible to activate the industrially more interesting aryl chlorides at 170 °C; moreover, a diminished formation of side products in the reaction of 4-Br-acetophenone with cyclohexene has been ascribed to zeolite shape-selective effects. The heterogeneity of these catalysts has only been evaluated by monitoring the filtrate activity *after reaction completion*. This cannot exclude participation of dissolved Pd species and subsequent recapture by the support.[77] Additional research has shown that in dimethylacetamide partial Pd dissolution from the zeolites does indeed occur; however, if the Pd-zeolite reactions are conducted in toluene and with organic amines as the

Table 1. Catalytic Performance of Heterogeneous Heck Catalysts in DMA

R^1	X	R^2	catalyst	time (h)	*T* (°C)	base	trans (%)[b]	cis (%)[c]	1,1- (%)[d]	ref
F	Br	Ph	$Pd(NH_3)_4^{2+}/Y$	20	100	NaOAc	92.5	0.7	6.5	76b
F	Br	Ph	$Pd(OAc)_2/Y$	20	100	NaOAc	57.6	0.4	3.9	76b
F	Br	Ph	$[Pd(C_3H_5)Cl]_2/Y$	20	100	NaOAc	74.2	0.5	5.2	76b
F	Br	Ph	Palladacycle/Y	20	100	NaOAc	1	nd[e]	nd[e]	76b
$COCH_3$	Cl	Ph	$Pd(NH_3)_4^{2+}/Y$	20	140	NaOAc	0.3	nd[e]	0.3	76b
$COCH_3$	Cl	Ph	$Pd(NH_3)_4^{2+}/Y$	20	170	NaOAc	44.1	1.2	3.3	76b
F	Br	Ph	Pd(0)/NaY	20	140	NaOAc	89.4	0.9	8.2	76a
F	Br	Ph	Pd(II)/NaY	20	140	NaOAc	90.2	1	8.4	76a
F	Br	Ph	$Pd(NH_3)_4^{2+}/Y$	20	140	NaOAc	90.4	1	8.6	76b
H	Br	Ph	$Pd(NH_3)_4^{2+}/NaY$	20	140	NaOAc	84.9	0.7	6.5	76b
H	Br	Ph	Pd-TMS11	48	170	NEt_3	39	0.5		80b
H	Cl	COOn-Bu	Pd-TMS11	32	170	NEt_3	16	0.2		80b
H	Br	COOn-Bu	Pd-TMS11	48	170	NEt_3	66	1		80b
NO_2	Br	COOn-Bu	Pd-TMS11	1.5	120	NEt_3	99	1		80b
$COCH_3$	Br	COOn-Bu	Pd-TMS11[f]	1	120	NEt_3	99	1		80b
NO_2	Br	Ph	Pd-TMS11	8	120	NEt_3	94	4		80b
$COCH_3$	Br	Ph	Pd-TMS11	0.75	120	NEt_3	94	5		80b
H	I	Ph	$MCM\text{-}NH_2{\cdot}Pd(0)$[g]	2	70	NEt_3	98	0		81[h]

[a] Reactions were performed with an aryl halide $R^1\text{-}C_6H_4\text{-}X$, an olefin $CH_2{=}CH{-}R^2$, and 0.1 mol % Pd, except as indicated otherwise. [b] Yield of the trans product. [c] Yield of the cis product. [d] Yield of the 1,1-disubstituted product. [e] Not determined. [f] 0.02 mol % Pd. [g] 0.3 mol % Pd. [h] Solvent is DMF.

base, the Pd is heterogeneous throughout the reaction.[78] While the reaction cycle might start from Pd(0) nanoparticles, the Heck mechanism requires Pd(II) intermediates, and it is conceivable that the latter stay well immobilized on an ion-exchanging support such as a zeolite. Pd-zeolites were also applied in a reaction related to Heck chemistry, viz. the α-arylation of diethylmalonate with *p*-substituted aryl bromides.[79]

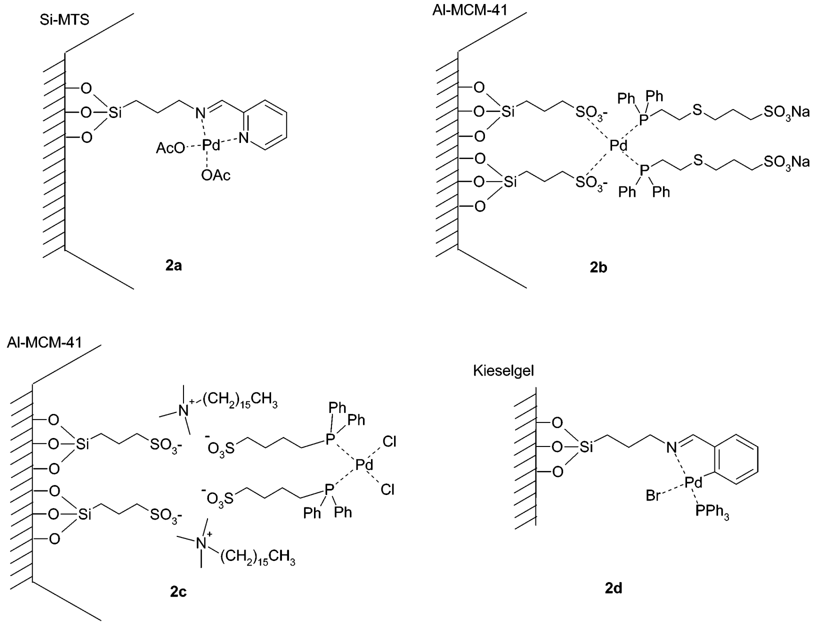
Pd(0) nanoparticles have been prepared by Ying et al. in the mesoporous siliceous material MCM-41, by adsorption and subsequent H_2 reduction of $[Pd(\eta\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$.[80] This procedure leads to a Pd(0) dispersion of 30%, and consequently, to a higher catalytic activity than with, e.g., Pd/Al_2O_3 or Pd/C. However, in the Heck reaction of bromobenzene with styrene, $Pd(NH_3)_4^{2+}/Y$ seems much more active at lower temperatures than the Pd-TMS-11 catalyst (Table 1).[76e] A strict leaching test for a reaction in dimethylacetamide gave no evidence for leached Pd. However, detailed TEM studies evidenced Pd agglomeration and structural damage to the support after use in catalysis. In a recent report, an aminopropylated MCM-41 was used as a support for Pd, but the resulting catalyst was only applied in a relatively easy reaction with an aryl iodide.[81]

B. Suzuki Reactions

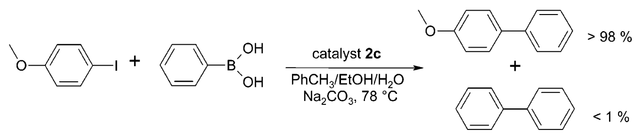
The Suzuki reaction is the Pd-catalyzed cross-coupling of *i.a.* arylboronic acids with aryl or alkenyl halides or triflates in the presence of a base.[82] Typical products are biaryls, which are often found as structural element in biologically active compounds (e.g., Rosoxacin, Diflunisal, the potent long-acting angiotensin II antagonist), in nucleoside analogues, in supermolecules and in liquid crystals.[82,83] As alternatives to the homogeneous Pd-phosphine catalysts, Pd/C,[84,85] silica or polymer supported Pd catalysts,[83a,86,87] and Pd on mesoporous materials can be used.[88,89] Various strategies have been followed for immobilization of Pd on mesoporous (alumino)silicates. Starting from an anchored aminopropyl group, Clark et al. prepared α-diimine groups on the surface of micelle-templated SiO_2 and Kieselgel; these can be metalated using a solution of $Pd(OAc)_2$ in acetone (catalyst **2a**, Scheme 19).[89] Alternatively, Kosslick et al. started from surfaces functionalized with propylsulfonic groups.[88] The alkylsulfonated support is prepared by bi- or tridentate anchoring of mercaptopropyltriethoxysilane (MPTS) on the walls of Al-MCM-41, followed by oxidation with hydrogen peroxide to the corresponding sulfonic acid. These functionalized supports are contacted with a mixture of $Pd(OAc)_2$ and a water-soluble phosphine ligand such as $Ph_2P(CH_2)S(CH_2)_3SO_3Na$, or with the preformed precursor $PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$ (catalyst **2b**, Scheme 19). Moreover, the alkylsulfonated Al-MCM-41 material may be amphiphilized by the adsorption of the surfactant cetyltrimethylammonium bromide (catalyst **2c**), followed by exposure to the same precursor complex. The quaternary ammonium ion not only changes the surface polarity, but also serves as phase transfer agent in the Suzuki reaction.[88]

The phosphine-free, diimine-based catalyst **2a** has been applied to the coupling of phenylboronic acid with bromobenzene in xylene with K_2CO_3 as the base. In this reaction, the filtrate is free of any residual activity. The use of the ordered, mesoporous support does not seem to offer obvious advantages over an amorphous SiO_2 support. Reactions with two liquid phases and a solid catalyst were performed using the sulfonated materials **2b** and **2c**. For instance, *p*-iodoanisol was reacted with phenylboronic acid in a biphasic toluene/ethanol/water mixture, with Na_2CO_3 as base and with the amphiphile cetyltrimethylammonium bromide (CTAB) as phase transfer agent (Scheme 20). The amphiphilized catalyst **2c** displays a much enhanced activity in comparison with the parent catalyst **2b** (90% conversion versus 2% conversion in 10 min). This was ascribed to a micellar effect, with the amphiphilic solid improving the mixing of the two liquid phases. However, a subsequent run with **2c** revealed a decreased activity,

Scheme 19



Scheme 20



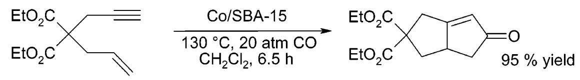
possibly due to loss of the quaternary ammonium compound from the support.

With above-cited catalysts, the active species may not only be the anchored Pd(II) complexes, but also deposited Pd(0) clusters, formed by decomposition of Pd(II) reaction intermediates. Experiments with silica-supported imine palladacyclic complexes such as **2d** (Scheme 19) have shown that small Pd(0) clusters are likely the active catalysts in many Suzuki reactions.[86] While catalysts **2a** and **2c** require activated aromatics such as bromides or iodides, recent reports indicate that conventional hydrogenation catalysts such as Pd/C or even Ni/C are capable of catalyzing Suzuki reactions with unactivated aryl halides such as chlorobenzene.[84,85,90] Therefore, the catalytic potential of phosphine-free, molecular sieve-supported Pd species certainly deserves further exploration.

C. Pauson-Khand Reaction

The term "Pauson-Khand" is used to include all reactions between carbon monoxide, alkenes, and alkynes that lead to the formation of cyclopentenone derivatives. The first *catalytic* Pauson-Khand reactions used homogeneous $Co_2(CO)_8$.[91] While this compound and its analogues are highly active, they are also volatile, toxic, and unstable due to loss of carbon monoxide and to oxidation. As heterogeneous Pauson-Khand catalysts, cobalt on charcoal or on mesoporous silica has been proposed.[92,93] In the latter catalyst, the cobalt is incorporated in the mesopores of SBA-15 and MCM-41 by decomposition of $Co_2(CO)_8$ in a refluxing toluene solution; metallic Co is formed. A more promising catalyst preparation for large-scale application is the classic impregnation of cobalt nitrate on SBA-15, followed by a H_2 reduction at 650 °C. This method avoids the expensive and toxic $Co_2(CO)_8$. Both Co/SBA-15 and Co/MCM-41 (10 wt % Co) exhibit excellent activity in the intramolecular Pauson-Khand reaction of allylpropargyl diethylmalonate in CH_2Cl_2 at 130 °C under 20 atm of CO pressure (Scheme 21). In these reactions, 13 mol % of the Co catalyst is used with respect to the substrate molecule. The yield of the bicyclic cyclopentenone product is 95−98% in 6.5 h, which compares favorably with homogeneous $Co_2(CO)_8$. With the same amount of cobalt on amorphous silica gel, 23 h are required for a yield of 83%. The superior performance of the mesoporous catalyst probably originates from a higher Co dispersion or a better access to the pore structure. Co leaching was not detected. Results for intermolecular cycloadditions, e.g., with norbornene, phenylacetylene, and CO, are however somewhat disappointing; possibly selective adsorption of one of the reagents results in a depletion of an other reagent at the active site.

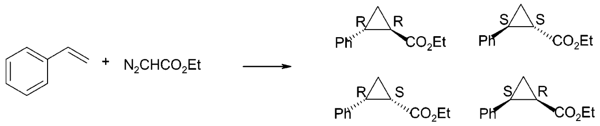
Scheme 21



D. Cyclopropanation

The direct transfer of carbene from diazo compounds to alkenes is the most straightforward route to cyclopropanes, which are common structures in pyrethroid insecticides.[94] In the cyclopropanation of, e.g., styrene with ethyl diazoacetate, four stereoisomers can be formed, indicating that both cis-trans selectivity and enantioselectivity are important (Scheme 22; Table 2). Homogeneous Cu salts generally provide high *trans*-selectivity in the reaction of diazo esters with olefins.[95] Upon exchange of Cu ions in zeolites, no significant deviations from this trans selectivity are observed (trans/cis ∼ 2; Table 2).[98] To

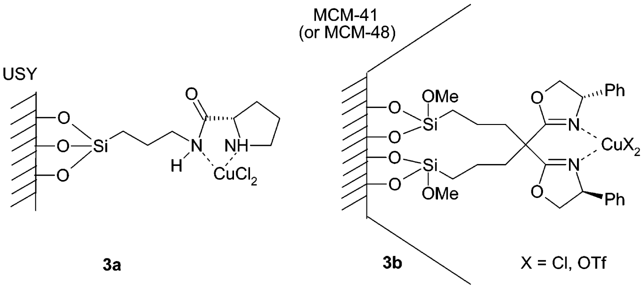
Scheme 22



obtain the less favored cis-isomer, specific homogeneous catalysts can be applied, e.g., substituted salen or porphyrin complexes of Co, Ru, or Rh;[96,97] or the classical Cu catalyst may be immobilized on a montmorillonite clay.[98] Cu on montmorillonite also displays a significantly higher activity in the styrene cyclopropanation than Cu-zeolites. An additional problem with many catalysts, including Cu-zeolites, is that the yields based on ethyl diazoacetate are lowered by dimerization to diethyl maleate and diethyl fumarate.[98,99] Moreover, to minimize the acid-catalyzed cationic polymerization of styrene, the free silanol groups of the supports have been deactivated by silylation with Me_3SiCl.[94,98]

In an early attempt to induce enantioselectivity, chiral ligands such as L-valine or (*R*)-1,2-propanediamine were added to NaCuX zeolites.[94] However, only very modest ee's (<2%) were observed in the cyclopropanation of 1,1-dichloro-4-methyl-1,3-pentadiene with ethyl diazoacetate. In another approach, Corma et al. used proline-derived chiral ligands, anchored to a mesoporous ultrastabilized Y-zeolite, in combination with Cu and Rh (**3a**, Scheme 23).[100] However, much lower ee's were obtained with the zeolite-anchored complexes than with their homogeneous counterparts (Table 2). With the zeolite-anchored complexes, the selectivity for the smaller *cis*-cyclopropane carboxylate is higher than with the homogeneous complex, which was ascribed to the steric effects of the microenvironment of the ligand−metal complex.

Scheme 23



Better enantioselectivities have been achieved by Clarke et al. with Cu complexes of optically active bis(oxazolines) tethered on the surface of MCM-41 and MCM-48.[101] The methylene spacer between the two oxazoline rings was used as an attachment point for alkoxy Si groups. It is indeed known from homogeneous catalytic studies, that substitution on the methylene bridge has only little impact on the enantioselectivity.[95a] Using a tethered 4,4′-diphenyl-bis(oxazoline) ligand and Cu(II) (**3b**, Scheme 23), the same enantioselectivities were obtained as with the corresponding homogeneous Cu(II) complex. Reuse of the chiral Cu-MCM-41 catalyst showed only a small drop in ee. However, it is unfortunate that the reactions were performed with 4-phenyl-substituted oxazolines; with these ligands, ee's are typically lower (∼ 40−50%) in the benchmark reaction of styrene with ethyl diazoacetate than with the chiral 4-*tert*-butyl substituted oxazolines (ee's 97−99%).[95a] Hence, it seems that attachment of the right ligand to an appropriate support such as MCM-41 leaves ample space for development of even better heterogeneous enantioselective cyclopropanation catalysts.

E. Diels Alder Reaction

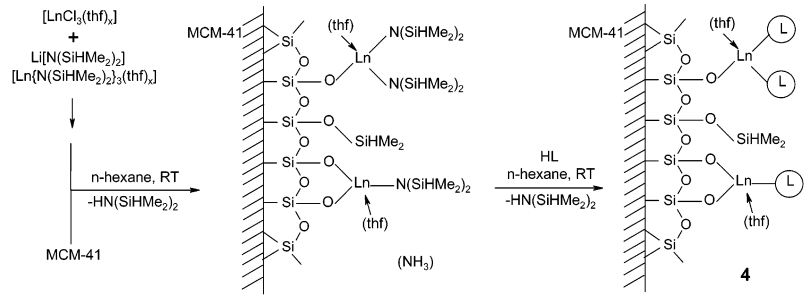
The use of Cu(I) loaded faujasite catalysts in Diels Alder reactions goes back to the early 70s. For the cyclodimerization of butadiene to 4-vinylcyclohexene in hydrocarbon solvents at 95−100 °C and elevated pressure, the best catalyst stability is obtained via direct exchange of monovalent Cu in zeolite Y.[102] The main role of the faujasite framework is to stabilize the Cu(I) ions; the 99% selectivity of the reaction is essentially the same as with homogeneous Cu(I) triflate. If the catalyst is prepared by mild reduction of Cu(II) zeolites, the Brönsted acidity generated by the reduction causes deactivation through deposition of polymers of butadiene; but with NH_3 as the reducing agent, the surface acidity is neutralized and the catalyst stability is enhanced. If the catalyst is regenerated by polymer burn off at high temperature, part of the Cu may be deactivated by formation of inactive CuO, particularly if the catalyst is prepared by direct exchange of Cu(I).[103] For optimum performance, a slightly hydrated Cu(I) zeolite should be

Table 2. Stereoselectivity in Cyclopropanation of Styrene with Ethyl Diazoacetate and Various Catalysts

catalyst	mol % metal	*T* (°C)	trans/cis	ee trans (%)	ee cis (%)	ref
Cu(II)/Y (pretreated at 120 °C)	1.71	50	2			98
Cu(II)/Y (pretreated at 550 °C)	1.71	50	1.7			98
Cu(II)-K10 montmorillonite (120 °C)	0.27	25	0.8			98
Cu(II)-K10 montmorillonite (EC[a])	0.27	50	1			98
Rh-TPP−I[b]			0.88			96
Ru-salen			0.03		>97	97a
Cu(II)-tButyl-(*S*)-prolinamide	0.67	25	1.88	13	10	100
Cu(II) and (*S*)-prolinamide anchored in US−Y	0.67	25	1.13	<5	<5	100
Cu(I)-bis(oxazoline)[c]	1	25	2.70	99	97	95a
Cu(II)-bis(oxazoline)[d]	1	25	2.05	58	49	101
Cu(II)-bis(oxazoline)[d]/MCM-41	0.24	25	1.95	51	46	101
idem, second run			1.78	45	42	101

[a] EC = end capped. [b] Rh-tetraphenylporphyrin. [c] 4,4′-*tert*-Butylsubstituted bis(oxazoline). [d] 4,4′-Phenyl substituted bis(oxazoline).

Scheme 24



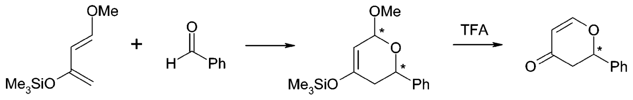
with Ln = Sc, Y or La
L = *e.g.* fod

used;[104] too strong dehydration causes migration of the Cu into the hexagonal prisms or sodalite cages to which butadiene has no access. This ion migration can be prevented by co-exchange with Ca, which preferentially occupies the sites in the hexagonal prisms and forces Cu back to the faujasite supercages. The reaction is also successful with Cu(I)-ZSM-12,[105] but fails with Cu(I)-ZSM-5 because of a too small micropore diameter.[106] The Cu(I) ion exchanged Y-zeolites also catalyze the Diels Alder reaction of furan, cyclopentadiene, and 1,3-cyclohexadiene with α,β-unsatured carbonyl compounds.[107] In the reaction of furan with methylvinyl ketone in CH_2Cl_2 at 0 °C, the cycloadduct is obtained with an exo/endo selectivity of 2.5:1, which is essentially the same as with other catalysts such as an Fe-exchanged bentonite clay. However, reversed stereoselectivities have been reported for reactions using a combination of Ce–Y zeolite and anhydrous $ZnBr_2$ as the catalyst.[108a] In the cycloaddition of cyclopentadiene with methyl acrylate or acrolein, a complete *endo* selectivity is achieved; however, the main disadvantage is that more than 0.7 g of zeolite is used per gram of reactants and per hour. Similar high *endo* selectivities are more easily obtained with homogeneous $AlCl_3$ and solid acid catalysts.[108b,c]

Heterogeneous hetero Diels–Alder reactions have been explored using organolanthanides grafted on modified mesoporous MCM-41.[109,110] Anwander et al. proposed an original "silylamide route" for functionalization of the siliceous surface with catalytic metal ions (Scheme 24).[109–111] In a first step, isolated silanol groups on the MCM-41 surface react with silylamide complexes $[Ln\{N(SiHMe_2)_2\}_3(thf)_x]$ (Ln = La, Sc, or Y), forming stable siloxide linkages between the metal and the support. Simultaneously, the released silylamines perform an end-capping with formation of hydrophobic $-OSiHMe_2$ sites. The second step is the intraporous ligand exchange reaction of the hybrid catalyst $[MCM\text{-}41]Ln\{N(SiHMe_2)_2\}_x(thf)_y$ with various ligands such as Hfod (Hfod = 1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6-octanedionate).[109,110] The resulting materials (6.0–7.0 wt % Ln, 0.2 mol % Ln) catalyze the asymmetric hetero-Diels–Alder cyclization of Danishefsky's diene (*trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene) with benzaldehyde in *n*-hexane at room temperature to form **5a** (Scheme 25). Product **5b** is obtained after acidic workup with trifluoroacetic acid (TFA).

The heteroleptic, surface-grafted complexes such as **4** (Scheme 24) have a more stable activity than the homoleptic homogeneous complexes such as $[La(fod)_3]$. This is *i.a.* due to the high-dispersion of well-defined surface complexes. Catalyst **4** is moreover free of metal leaching. The combined steric constraints of the surface and the ligand can induce enhanced diastereoselectivity in product **5a**, or if a chiral ligand such as BINOL is used, a significant enantioselectivity in the eventual product **5b**.

Scheme 25



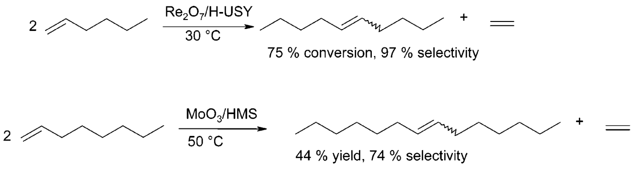
5a **5b**

F. Metathesis

The new generations of homogeneous metathesis catalysts as described by Schrock, Grubbs, and others are often tungsten, molybdenum, or ruthenium alkylidene complexes.[112] Heterogeneous variants of Grubbs' Ru carbene catalyst have been developed by chemical attachment to a carbosilane dendrimer,[113] by binding of Ru to a polymer-bound phosphine ligand,[114] or to a polymeric carbene ligand.[115] In another approach, zeolites or ordered mesoporous molecular sieves may be worthwhile alternatives for the amorphous carriers that are employed in traditional industrial metathesis catalysts such as WO_3, Re_2O_7, or MoO_3 on alumina.[116–118]

For example, a metathesis catalyst was prepared by impregnation of a dealuminated Y zeolite with NH_4ReO_4 followed by calcination.[117] In the presence of the cocatalyst Me_4Sn, this material catalyzes 1-hexene metathesis at 30 °C in chlorobenzene (Scheme 26):

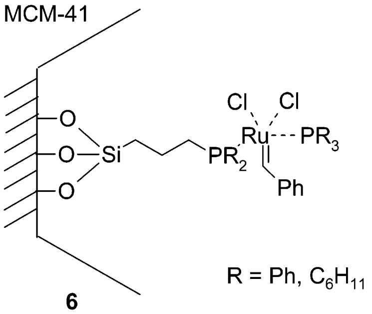
Scheme 26



The equilibrium composition is reached much faster than with the same amount of Re dispersed on γ-alumina. The Brönsted acid sites and the extraframework Al species seem to play a role, respectively, in increasing the activity and suppressing side reactions such as isomerization. Similar beneficial effects of a mesoporous support have been observed for MoO_3 clusters dispersed in HMS materials with varying pore diameters and particle dimensions.[118] The activity of MoO_3/HMS far exceeds that of MoO_3 on amorphous carriers, for instance, in the 1-octene metathesis to 7-tetradecene, and no cocatalyst is needed with MoO_3/HMS (Scheme 26). A large pore diameter of the HMS support results in a high initial activity due to easy reactant diffusion, while catalysts based on small particles with shorter channels seem more resistant to deactivation by pore blocking. However, details on catalyst recycling or metal leaching have not been provided for the Re_2O_7/H-USY catalyst nor for the MoO_3/HMS system.

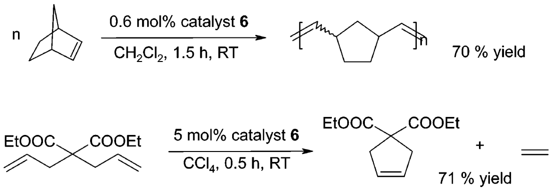
Finally, Grubbs' catalyst was anchored on MCM-41 by ligand exchange between a covalently linked phosphine and the PR_3 ligand of the catalyst complex $(R_3P)_2Cl_2Ru{=}CHPh$ (R = Ph) (Scheme 27).[116] This exchange is favored by the stronger donor capacity of the anchored alkyldiphenylphosphine in comparison with PPh_3. In the ring opening metathesis polymerization (ROMP) of norbornene, satisfactory activity is observed for the heterogenized Grubbs catalyst, but the polydispersity index of the formed polymers (PDI ∼ 7) is much higher than with the homogeneous catalyst (PDI 1.04−1.10) (Scheme 28).

Scheme 27



6

Scheme 28

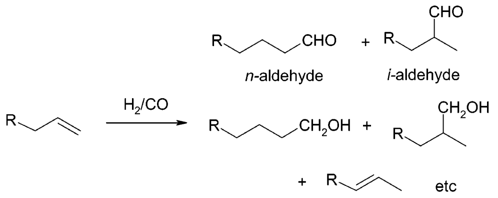


Since the phosphine ligands are isolated over the MCM-41 surface, different Ru speciations due to multiple phosphine coordination are unlikely;[114] rather, diffusion limitations may explain the lower activity of Ru complexes anchored inside the pores and the ensuing polymer polydispersity. With catalyst **6**, the ROMP can even be conducted in an aqueous environment, which is not possible with the homogeneous catalyst due to insolubility. The same catalytic system is also active in the ring closing methathesis (RCM) of diethyldiallylmalonate in CCl_4 (Scheme 28), but the reaction is slower than with the homogeneous catalyst, again because of diffusion limitations. During reaction, a few % of the Ru leaches to solution, but it can be expected that at the end of the reaction, much Ru is recaptured on the support in a "boomerang" effect.

G. Hydroformylation

Whereas the hydroformylation of alkenes preferably into *n*-aldehydes (Scheme 29) is one of the largest processes today running on Rh or Co catalysts, it still suffers from the usual drawbacks of homogeneous catalysis. As metal (and ligand) recovery and metal regeneration are energy- and time-consuming,[119] attempts to heterogenize catalysts remain relevant. Literature only reports work on Rh-based catalysts. Apart from zeolites, clays have been frequently used as a support, both for liquid and gas-phase hydroformylation catalysis. Success with clays has been mixed.[120] For instance, stable activity in a series of consecutive runs was claimed with a $Rh(PPh_3)_3^+$/montmorillonite catalyst in the liquid-phase hydroformylation of allyl alcohol,[120a] but in hexene liquid phase hydroformylation, loss of a neutral Rh−phosphine complex from the support was reported. Although the catalysts show acceptable activity and selectivity for aldehydes and moderate regioselectivity (*n*-/*i*-aldehydes), the available data do not allow one to evaluate whether clays are generally applicable as supports in Rh-catalyzed hydroformylations.

Scheme 29



1. Phosphine-Free Rh Zeolites

It has been hoped that the action of zeolites as polydentate ligands would allow one to stabilize specific catalytic species and to induce stereochemical control of the regioselectivity. Among the procedures for preparation of Rh-zeolites, dilute aqueous exchange at room temperature with $RhCl_3$ or $Rh(NH_3)_5Cl_3$ is most popular.[121] In large-pore zeolites such as Y and mordenite, Rh can be uniformly distributed across the zeolites, while medium pore size zeolites (ZSM-34 and ZSM-11) show rhodium enrichment at the surface due to hydrolysis. In small pore zeolites (e.g., erionite, zeolite A, ZK-5) surface hydrolysis dominates, and most rhodium is found on the external surface.[121] Depending on the pretreatments of these zeolites, e.g., calcination, autoreduction, reduction at various temperatures, under H_2 or CO, various species can be formed, e.g., lattice-coordinated Rh^{3+}, RhO_2, or Rh_2O_3 particles, metallic Rh^0 clusters, or carbonyl complexes such as $Rh^I(CO)_2$ or $Rh_6(CO)_{16}$.[121] These zeolites have been applied for gas and liquid-phase reactions.[122,123] As an example, gas-phase hydroformylation of 1-hexene was performed with a zeolite CaA synthesized in the presence of Rh.[122h] Enhanced selectivity for the *n*-aldehyde was observed in comparison with an exchanged zeolite,

Table 3. Liquid Phase Hydroformylation of 1-Hexene[a] with $Rh^I(CO)_2$/NaY[125]

ligand	[Rh] (ppm)[b]	conversion (%)	aldehyde selectivity (%)	regio-selectivity (n/i)	Rh-elution (%)
	242	52	53	2.0	0.5
PMe_2Ph	238	2	18	2.1	0
$PMePh_2$	260	50	75	2.2	0.04
$P(n\text{-}Bu)_3$	323	11	77	2.4	1.9
$P(t\text{-}Bu)_3$	318	87	68	2.0	1.6
PPh_3	318	24	89	2.8	0.04

[a] At 50 °C/2.1MPa (CO/H_2= 1). [b] Total concentration in reaction medium.

but loss of volatile Rh-carbonyls resulted in a gradually decreasing activity.

Liquid phase 1-hexene hydroformylation was investigated with $Rh(NH_3)_5Cl^{2+}$ exchanged NaY zeolite after carbonylation treatment. This material contains $Rh_6(CO)_{16}$ clusters associated with the zeolite crystals. This catalyst was characterized by a high hydroformylation selectivity and a lack of regioselectivity. This is very similar to the behavior of homogeneous rhodium carbonyls, which were found to be present in the reaction mixture.[123a] While for Rh^{III}-exchanged NaY and CaA the observed activity is caused by eluted rhodium,[122h] experiments with poisons and additives allowed the speculation that *i.a.* NaX zeolites exchanged with $Rh(NH_3)_5(H_2O)Cl_3$ are a source of homogeneous as well as heterogeneous activity.[123b,c,121h] At high reaction temperatures, leaching from the zeolite decreased, possibly due to the formation of larger Rh clusters that are difficult to be converted into soluble species.[123b] Unfortunately, under such conditions, the chemoselectivity is largely in favor of substrate isomerization, probably catalyzed by residual zeolite acidity.

2. Rhodium-Phosphine Complexes in Zeolites: The Ship-in-a-Bottle Approach

The bulky nature of the phosphine ligands makes entrapment of their rhodium complexes in zeolites cages a difficult task. A computational study revealed that phosphine ligands with more than one aromatic substituent are not able to diffuse into the pore system of zeolite Y.[124a] Only a few examples of rhodium−phosphine complexes inside zeolites have been reported. Intrazeolitic rhodium carbonyl clusters are able to react with small phosphines such as dimethylphenylphosphine. When larger molecules such as triphenylphosphine and tris(2-cyanoethyl)-phosphine are used, a species such as $Rh^I(CO)_2$ probably migrates to the outer surface to react with the phosphine.[124b]

Compared to $Rh_6(CO)_{16}$/Na-Y, zeolite Y entrapped Rh−dimethylphenylphosphine complexes in propene hydroformylation show a higher n/i ratio (2.00 vs 1.75). However, the catalyst is completely deactivated after 24 h.[122c] With other Rh−zeolite−phosphine complexes, similar increases of the n/i ratio have been observed.[124c] With triphenylphosphine ligands, selectivity to aldehydes improved, while the high regioselectivity was retained. However, a small loss of rhodium was detected.[121c] Some typical results are given in Table 3. It is clear that only at the very low substrate conversions, no leaching of Rh into the reaction medium is encountered. Whereas the hydroformylation selectivity is acceptable, the regioselectivity is moderate. It further seems that activity and leaching are dependent on reaction conditions and nature of the phosphine ligand.

In recent work, it seems that truly heterogeneous hydroformylation with such zeolite-based catalysts is possible, though no specific evidence for the absence of leaching was offered.[125a,b] Stable hydrocarbonylation of unsaturated compounds seems possible at 120 °C and 5 MPa. In ethanol, primary alkylphosphines promote formation of alcohols. This is due to the proton-donating ability of ethanol, facilitated by strongly electron-donating phosphines such as triethylphosphines, resulting in the formation of hydroxycarbene species from acyl intermediates. If toluene is used as a solvent, or if triphenylphosphine is used in place of more basic alkylphosphines such as triethylphosphines or tripropylphosphines, a mixture of aldehydes and *n*-alkanols is formed.[125a,b] Generally speaking, a higher regioselectivity for linear products (n/i) was obtained compared to the homogeneous counterparts, though the use of zeolite supports resulted in a decreased activity.

Sulfur ligands more stable toward oxidation and degradation than P-ligands have been used for comparative purposes as well. However, the stability advantage is balanced by activity and selectivity loss. $Rh^I(CO)_2$-zeolites with faujasite and Beta topology were contacted with S-ligands via diffusion and via intrazeolite ligand synthesis. Although the regioselectivity was rather low, claims for good reusability and negative filtration tests were presented.[125b]

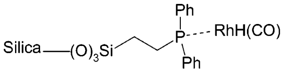
3. Zeolite Pore Mouth Adsorption of Rh-Phosphine Complexes

As Rh−phosphine complexes are sometimes too large to diffuse inside zeolites, they can at best interact with the external surface and the pore mouths of the crystals. An example of "pore mouth sorption" in the aqueous (bi)phase hydroformylation of propene, concerns a NaY immobilized 2.0 nm $Rh_{55}L_{12}Cl_6$ cluster ($L = P(tBu)_3$, $x = 20$; $L = PPh_3$). This cluster is adsorbed on NaY, blocking its micropores. The catalyst could be reused 27 times without deactivation, while turnover frequencies in the range 400−600 mol propene mol^{-1} Rh min^{-1} were possible with an n/i ratio of 1.0 (30.0 MPa $CO/H_2 = 1$, 120−130 °C).[125c] It is not clear at this moment whether the catalyst stability is the result of the interaction of the cluster with the zeolites pore mouths rather than of the biphasic reaction conditions.

4. Silica-Tethered Rh-Phosphine Complexes as Reference

Introduction of groups amenable to covalent linking on phosphines is difficult and explains why only a limited range of silica-anchored phosphines has been reported. Silylation is often accompanied by side reactions involving transformation of part of P^{III} into P^V, but this oxidation can be avoided in specific reaction conditions. The possibility of using rhodium on phosphinated silica as hydroformylation catalyst was already considered in the 1970s.[125e] Silica anchored $RhH(CO)((Ph_2P(CH_2)_2Si(C_2H_5O)_3)_3$ in rhodium catalyzed hydroformylation of 1-hexene was claimed to show good activity and stability (Scheme 30).

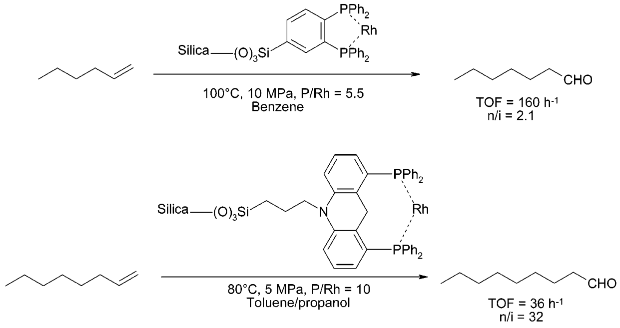
Scheme 30



Rhodium elution was only observed during the first hours.

More recently anchored bidentate phosphines have been used (Scheme 31).[125f,g] Such heterogeneous catalysts could be used for 14 days without loss of activity.[125f] The rigid backbone with large bite-angle seems responsible for the high *n*/*i* ratio of 32. Whereas such systems are more difficult to prepare, their performance by far outpasses that of all previously described systems. With the present knowledge on structured mesoporous silicas, this performance might still be susceptible to further major improvement.

Scheme 31



IV. Reductions

Besides the numerous early reports on transition metal cation exchanged zeolites,[126] immobilization of organometallic complexes is by far the most popular strategy to date toward heterogenized hydrogenation catalysis. Although it may be difficult to surpass the success of commercial catalysts such as Raney nickel, Pd on C, and Pt on alumina, supported homogeneous catalysts are especially promising when aspects such as catalyst poisoning and product selectivity, e.g., enantioselectivity, are decisive. Notwithstanding the relative newness of this research area, publications on supported homogeneous catalysts are numerous. Within this area, zeolites and mesoporous materials are often attractive candidates for use as support. Due to their regular pore size, they sometimes offer unexpected advantages for the hydrogenation activity or for the selectivity of the hydrogenation process. So far, supported porous materials have been used in the hydrogenation of, e.g., alkenes, arenes, enamines, ketones, and nitro compounds.

A. C═C Hydrogenation

1. Ship in a Bottle or Tea-Bag Approach

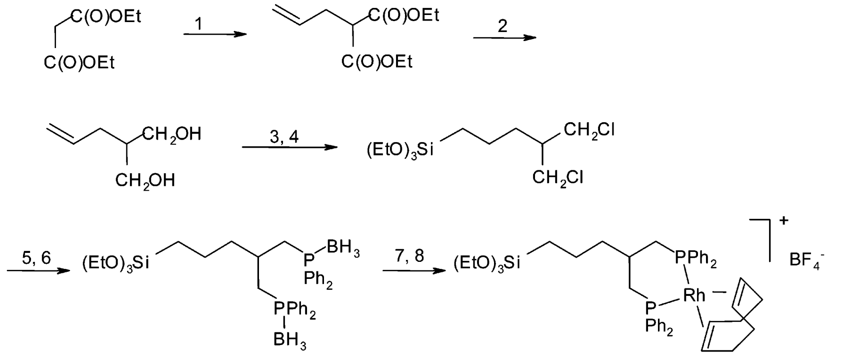
Homogeneous metal complexes—the ship—can be introduced in the cages of a zeolite—the bottle. Although most examples of this immobilization technique are found in the area of oxidation chemistry (cfr. II), hydrogenation catalysts have been reported as well.[127] Entrapment in zeolites often leads to special effects on, e.g., selectivity or substrate specificity. For instance, in the hydrogenation of 1-octene, less isomerization to internal olefins was observed for the Pd-salen-NaY catalyst in comparison with Pd loaded Y zeolite or Pd/C.[127c] For the hydrogenation of butadiene with iron phthalocyanine Y zeolite (FePc-NaY) in a continuous flow reactor, a small preference for *trans*-2-butene was obtained, whereas the original crystalline complex preferentially yields the cis isomer.[127a] In another example, size discriminating effects have been observed with zeolite encapsulated salen complexes (salen: *N*,*N*′-bis-(salicylidene)-ethylenediamine). In the competitive hydrogenation of 1-hexene and 2,4,4-trimethylpent-1-ene, conversion of the linear olefin is strongly preferred over that of the bulky olefin with the encaged complex, while both olefins are reduced with a comparable rate in the presence of the soluble Pd-salen.[127e] Size exclusion is not a distinctive ship-in-a-bottle feature, as similar observations have been reported for zeolites loaded with Pt and Pd clusters.[128]

In principle, asymmetric hydrogenation of prochiral substrates might be possible when chiral salen complexes are introduced in the zeolite. However, no attempt so far meets the high demands of state-of-the-art enantioselective hydrogenation. For instance, the chiral Pd complex of (*R*,*R*)-*N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine has been encapsulated in the large cages of FAU and EMT zeolites; the resulting supramolecular assemblies were used in the double bond hydrogenation of 3-methyl-2-cyclohexenone.[129] The EMT type catalyst is much more active than the FAU derived catalyst. However, for both catalysts, enantiomeric excesses of (*R*)-3-methylcyclohexanone never exceeded 7%.

2. Covalent Approach

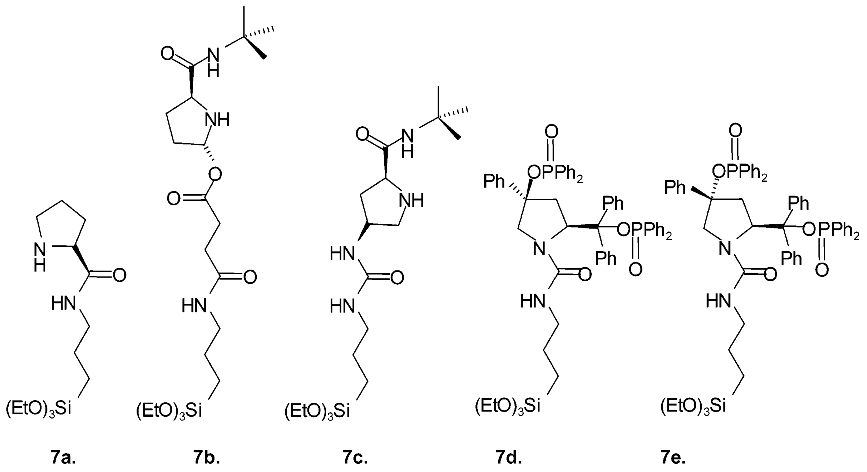
More recently, supported hydrogenation catalysts have been obtained by immobilizing active soluble complexes via covalent bonding. Key challenge for this heterogenization methodology is to find broadly applicable and efficient ligand modifications affording metal complexes with appropriate docking points. Many examples have been published. A nice illustration of simplicity is given by Shyu et al.[130] In their report, the Wilkinson complex, a well-known homogeneous catalyst for olefin hydrogenation, was immobilized in the mesopores of MCM-41 via complexation with chemically bonded phosphinopropyl ligands. Specifically, MCM-41 was treated with commercial $(EtO)_3Si\text{-}(CH_2)_3\text{-}PPh_2$ and then with $Rh(PPh_3)_3Cl$. The catalytic potential of the supported Rh was evaluated in the hydrogenation of cyclohexene. Up to ca. 7200 cycles per hour were observed, i.e., three times higher than that of the free metal complex. This is rather unexpected since most reports on immobilized homogeneous catalysts generally report a decrease in activity. No explanation was given by the authors why the hybrid catalyst was so active. Moreover, the

Scheme 32[a]



[a] (1) Alkylation with allylbromide (89% yield). (2) Reduction of the ester groups with $LiAlH_4$ (69% yield). (3) PPh_3/CCl_4 (69% yield). (4) Hydrosilylation with $HSiCl_3$ using H_2PtCl_6, then EtOH and NEt_3 (yield 72%). (5) Introduction of the phosphine substituents using Ph_2PH and *n*-BuLi. (6) Protection by $BH_3{\cdot}SMe_2$ (yield 56%). (7) Deprotection with morpholine. (8) Treatment with $[Rh(COD)(THF)_2]^+BF_4^-$.

Scheme 33



catalyst could perform over 10^6 catalytic cycles, and was recycled without activity loss.

Similar catalysts have been prepared by Liu et al. by complexing $[Rh(CO)_2Cl]_2$ on phosphinated and aminated MCM-41.[131] The hybrid Rh materials were highly active as catalysts in the hydrogenation of arenes in extremely mild conditions. The hydrogenation activity of the Rh phosphine was superior to that of the Rh amine complex. Reactivity patterns were comparable with those of homogeneous reactions. Thus, methyl substituents on the aromatic nucleus drastically reduce the reactivity of the substrate; mesitylene, for instance, is a less suitable substrate than benzene. No hydrogenolyzed, cracked, or partially reduced products were analyzed, and the solid catalyst was reused several times with only minor loss of activity. Leaching of the Rh complex in solution was not observed.

Crudden et al. developed a more sophisticated procedure for the preparation of a MCM-41 grafted bidentate rhodium phosphine complex.[132] By using a cationic complex with bidentate phosphine ligands, it was attempted to minimize possible leaching and to increase activities by preventing dimerization of the Rh catalyst. In contrast to the previous examples, a multistep synthesis of the triethoxysilyl diphosphine moiety was followed (Scheme 32).

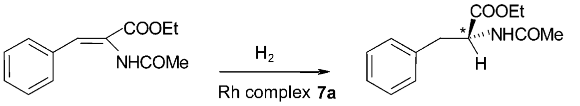
The system was tested in the hydrogenation of isosafrole at room temperature. The method of grafting was found to have an influence on both the catalytic activity and on complex leaching. The most active Rh catalyst is obtained when the anchoring procedure is performed at 25 °C in the presence of an inert spacer molecule $EtSi(OEt)_3$. Unfortunately, retention of Rh with this catalyst appears to be poor, despite the use of a chelating diphosphine. Up to 36% of Rh was leached out of the MCM-41 framework after the first cycle and ca. 5% in subsequent cycles. In view of the stability of the supported Wilkinson catalyst mentioned before, this is rather unexpected. Using a somewhat different grafting method in which the Rh complex is linked at 110 °C in absence of the inert silylation agent, the catalyst became more robust, leaking only 2−3% of Rh per cycle. However, improvement of catalyst stability came along with a decrease of the Rh activity by a factor of 2. The latter heterogeneous Rh catalyst was able to hydrogenate the olefin with a rate of 1600 turnovers per h at room temperature and 50 bar H_2. Catalytic lifetimes were not investigated.

New chiral *N*,*N*′-, *N*,*P*-, and *P*,*P*′-ligands for Rh, derived from L-proline and L-*trans*-4-hydroxyproline have been tethered to the internal surface of a mesoporous US-Y (Scheme 33).[133−135]

The catalytic behavior of Rh complexes of **7a**, **7b**, and **7c**, for instance, was evaluated in the hydrogenation of common olefins such as 1-hexene, cyclohexene, and 1-methyl-1-cyclohexene.[134] The reaction sequence in the anchoring procedure exerted no influence on the catalytic activity. Indeed, whether the catalyst was prepared by immobilizing the ligand followed by metalation, or by anchorage of the whole metal complex, did not influence the characteristics of the hydrogenation. The activity of the immobilized Rh-complexes was higher than that of the corresponding soluble complexes. Maximum turnover frequencies were 1000 to 1600 catalytic cycles per hour. Importantly, even after 10 recycles, no loss of hydrogenation activity was found.

The USY zeolite support did not only affect the activity and stability of the metal complexes; it also had an influence on the substrate reactivity and product selectivity. Intermolecular competition normally depends on the intrinsic reactivity of the olefin. However, it is known that when bulky ligands are wrapped around the metal, cyclohexene is often more rapidly converted than 1-methyl-1-cyclohexene because of steric restrictions. Due to geometrical constraints, substrate specificity can be even more pronounced in the confinements of the zeolitic material. A remarkable promoter effect of the zeolite on the enantioselectivity was observed when prochiral olefins were used.[133] The less bulky the prochiral olefin, the larger the difference in enantiomeric excess between the homogeneous and heterogeneous system. For instance, the supported chiral Rh complex with ligand **7a** was used for the hydrogenation of an α-acylaminocinnamate at 65 °C under 5 atm H_2 pressure yielding the corresponding phenylalanine quantitatively with ee values of 94%. In homogeneous conditions, ee's of only 54% were observed (Scheme 34).

Scheme 34



Improvement of enantiomeric excess upon heterogenization is not common. Since only minor improvements of ee were observed when using amorphous silica, well-ordered rigid pores of molecular dimensions are essential. Moreover, not every complex can be influenced in such a way as illustrated in the example above. For instance, when ligands **7d** and **7e** are tethered on USY and metalated with Rh, ee's are moderate and very similar to the results of the unsupported catalysts.[136]

Increased enantioselectivity upon immobilization can be explained tentatively by the confinement concept.[137] The key idea is an interaction of the substrate with the bulky chiral directing groups and with the walls of the support. Somehow this might change orientation of the substrate to the chiral center leading to improved enantioselectivity. The findings of the Thomas group were based on results obtained in the hydrogenation of ethyl nicotinate using a chiral Pd 1,1′-bis(diphenylphosphino)-ferrocene catalyst. While the hydrogenation with the soluble version of the catalyst resulted in a racemic mixture of the nipecotinate, a 17% ee was achieved when the chiral catalyst was confined in the inner space of M41S. Careful design of tailor-made catalysts using the inner space of mesoporous materials will probably lead to even more unexpected regio- and enantioselectivities soon.

3. Recent Noncovalent Approaches

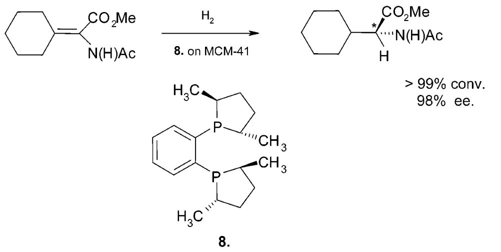
Due to the complexity of the covalent approach and due to the difficulties to apply this technique on large production scale, researchers have explored the potential of other immobilization methods. Physisorption of an existing soluble metal complex in the pores of a host is an interesting alternative for immobilizing homogeneous metal complexes. If the ionic and Vanderwaals interactions are strong enough to ensure retention of the complex during reaction, it is by far the easiest immobilization protocol. Crudden et al. briefly mention that simple mixing of $[Rh(COD)_2]^+BF_4^-$ with a mesoporous MCM-41 support in absence of any phosphine results in a hydrogenation catalyst with activities two times higher than the unsupported complex.[132] Although the heterogeneity of the hydrogenation was hardly checked, this example indicates that MCM-like materials are not only capable of holding cationic Rh complexes out of solution; the presence of a solid support also enhances the activity of the metal catalyst.

For obvious reasons, supported catalysts prepared by adsorption are more subject to leaching problems than covalently linked complexes. To maximize catalyst retention, closeness of fit of the catalyst, polarity of the support, temperature, concentration of the reagents, and nature of solvent become very crucial. Preferably, the metal complex is not soluble in the solvent used in the hydrogenation. Of course, this limits the use of the catalytic system with respect to the choice of substrates. The pore size of the HMS material is best adapted to the molecular dimensions of the complexes. For instance, in the hydrogenation of itaconic acid with Rh-BPPM and Ru-BINAP, Jamis et al. observed considerable leaching beyond 40% Rh and Ru when using unstructured gel-based silica, whereas only 4−5% of metal was detected in the end product for an 2.6 nm HMS based catalyst.[138] The authors attempted a further reduction of the metal losses by functionalization of the support with propylcarboxylate and aminopropyl entities. However, complete metal retention was never achieved.

To obtain a recoverable and nonleaching asymmetric hydrogenation catalyst, de Rege et al. reported that the nature of the counteranion was of tremendous importance.[139] While the Rh complex of triflate Duphos **8** was effectively retained by the MCM-41 support, loading with the same Rh phosphine complex containing a somewhat more lipophilic anion such as $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ appeared unsuccessful (Scheme 35).

It was suggested that retention of the complex is based on hydrogen bonding of the triflate with the surface hydroxyl groups. Nevertheless, although no metal was found when operating in hexane, leaching might be unavoidable if polar and protic solvents are used. The triflate Rh-MCM-41 catalyst led to high activities and ee's for the hydrogenation of prochiral enamides. The catalytic results of the supported

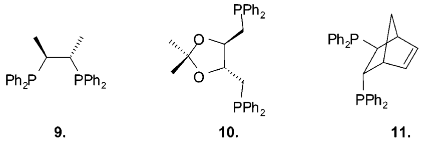
Scheme 35



catalyst sometimes surpassed those of the homogeneous analogue.

Recently various cationic diphosphine Rh complexes have been supported on nonmodified Al substituted MCM-41.[140] The catalysts were prepared by impregnating the carrier system with a chloride salt of the catalyst precursor in dichloromethane. That the complex is loaded onto the support was seen by a decoloration of the solution and the yellow color of the solid. Soxleth extraction was carried out with methanol to remove loosely bond organometallics. In this way, supported Rh catalysts were obtained with Rh contents varying between 0.02 and 0.07 mmol/g of Al−MCM depending on the complex used (Scheme 36).

Scheme 36



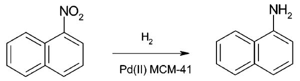
For instance, Al-MCM-41 supported Rh complexes of *S*,*S*-Me-Duphos **(8)**, *S*,*S*-Chiraphos **(9)**, *R*,*R*-Diop **(10)**, and (+)-Norphos **(11)** were studied in the asymmetric hydrogenation of itaconic acid. Supported ligand **8** gave the best results with 92% ee at 100% conversion of the dimethyl *R*-methylsuccinate. Conversions and ee's in this hydrogenation were followed through four cycles. Filtration fully recovered the solid catalyst. Analysis of the filtrate showed no residual catalytic activity. The authors proposed two binding mechanisms: either the cationic complex may be held by the support due to ionic interaction with the anionic structure of the Al-MCM-41, or rhodium is directly bridged with surface oxygen atoms. Duphos-Rh-MCM-41 is extremely stable and is able to operate for over 16 000 turnover numbers.

Zeolites have been impregnated with a solution of optically active metal BINAP complexes and used in the asymmetric hydrogenation of various olefins.[141] While considerable leaching was observed for most zeolite structure, a zeolite with *BEA topology surprisingly appeared to be unique in keeping the complex out of solution. Interestingly, the heterogeneous Ru-BINAP-H-Beta system was able to smoothly catalyze the hydrogenation of, e.g., ketoesters already at room temperature and 60 atm H_2 pressure. A supported phase containing sulfonated Ru-BINAP, for instance, did not show any activity, even in more drastic conditions such as 80 °C and 60 atm H_2 pressure. As an example, when Ru-BINAP-H-Beta is contacted with methyl acetoacetate at room temperature in ethylene glycol for 6 days, methyl (*R*)-3-hydroxybutanoate is formed with 95% ee at 80% conversion. Typical turnover frequencies are on the order of 0.1 min^{-1}.

B. Reduction of Nitro Compounds

A Pd complex immobilized on MCM-41 was studied in the mild reduction of aromatic nitro compounds.[142] The catalyst was prepared by complexation of dichlorobis(benzylcyano)palladium(II) on aminopropylated MCM-41. The material catalyzes the reduction of nitro compounds to the corresponding aromatic amines in high yields at room temperature and atmospheric H_2 pressure. Interestingly, since the Pd complex is embedded in large mesopores, also bulky substrates can easily be hydrogenated. As an example, 1-nitronaphthalene is quantitatively converted into the amine in THF with an overall rate of 60 mol of amine per mol of Pd and per h (Scheme 37). Complete reusability of the catalyst was claimed.

Scheme 37



C. Reduction of Carbonyl Groups

Immobilized transition metal catalysts have been used for the reduction of carbonyl groups using molecular hydrogen, alcohols, or borohydrides as reductants. For instance, pyruvate and acetoacetate esters were hydrogenated with H_2 to the corresponding hydroxy compounds using Pt salen complexes entrapped in a H-USY zeolite.[143] Occlusion of the Pt salen in the zeolite was essential for hydrogenation activity, as the soluble Pt salen showed no activity. The best results were obtained when the supported catalyst is prepared by sublimation of the salen ligand in ion-exchanged Pt-USY, instead of by impregnation of USY, alumina, or silica with a Pt salen solution. This example demonstrates the unique property of zeolites to immobilize and isolate complexes in their cages, thereby preventing the formation of inactive dimers or aggregates.

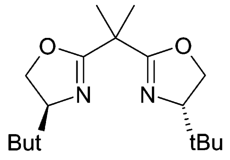
Chiral Co-salen complexes encaged in zeolites were used in the hydrogenation of carbonyls. Improvement of enantiomeric excess as a result of immobilization was reported.[144] Optically active Co-salen complexes were also anchored on the surface of MCM-41 using 3-aminopropyl spacer molecules. The supported catalyst was active in the asymmetric borohydride reduction of aromatic ketones, showing ee's higher than those obtained for the soluble complex.[145] There are also several examples of useful catalysts based on zeolites or MCMs for transfer hydrogenation. For instance, ketone reduction with 2-propanol as a reductant is possible with isomorphously substituted zeolites,[146] or with MCM-41 materials with metals grafted via the silylamide route (cfr. supra, Scheme 24).[109−111,147] In the reduction of 4-*tert*-butylcyclohexanone, the thermodynamically unfavored cis alcohol isomer is obtained using a Ti-Beta catalyst with relatively narrow pores; by contrast, in the more spacious channels of the MCM-41 structure with grafted Al, the larger trans isomer is obtained with high selectivity.[146,147]

V. Miscellaneous Reactions

A. Aziridination

Sulfonated aziridines are easily prepared from olefins using substituted imino-phenyliodinanes such as PhI=N-Ts (Ts = tosyl) or PhI=N−Ns (Ns = (*p*-NO_2-phenyl)sulfonyl). As an alternative for the standard homogeneous Cu triflate catalyst, Cu-exchanged zeolites have been proposed.[148,149] A first advantage of these zeolites over the homogeneous catalyst is that yields based on the nitrene donor are higher with CuY than with dissolved Cu. Apparently, less of the PhI=NTs is decomposed with CuY. Additionally, the reactions can be made enantioselective by addition of bis(oxazoline) ligands. EPR spectroscopy has revealed that a 1:1 Cu/ligand complex is formed.[149] Satisfactory ee's are observed even if the amount of ligand is much smaller than the Cu concentration. This may indicate that only the Cu ions in the outer rim of the zeolite crystals are active. Nevertheless, there is ample evidence that the reaction truly occurs inside the zeolite channels. With the $(CH_3)_2C$-bridged oxazoline **12** as a ligand (Scheme 38), an ee of 82% is achieved in the aziridination of styrene with PhI=N−Ns. This value is much higher than for $Cu(OTf)_2$ with the same ligand (43%). This enhanced enantioselection is ascribed to additional spatial constraints when the complex is formed inside the supercages. By comparison of reactions with styrene and stilbene, indications for shape-selective effects have been gathered. Detailed study of catalyst stability has shown that in proper reaction conditions, Cu leaching can be limited to levels that are irrelevant to homogeneous catalysis. In addition to aziridination, similar Cu-zeolites have found application in the amination of silyl enol ethers with PhI=N-Ts to form α-aminoketones.[150]

Scheme 38



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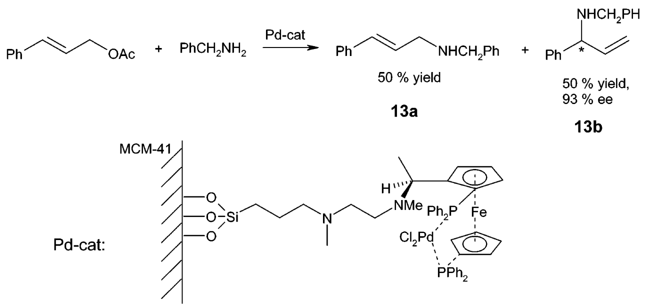
B. Allylic Amination

Another example of Thomas' confinement concept is found in the allylic amination of cinnamyl acetate with benzylamine.[137,151] Again, an MCM-41 with a tethered chiral bis(diphenylphosphino)ferrocene was metalated with Pd and used in the catalytic reaction (see IV. A.2). To exclude contributions from sites at the external surface, the latter was selectively deactivated with Ph_2SiCl_2 under "nondiffusive" conditions. In comparison with the related homogeneous catalyst or the Cab-O-Sil anchored complex, the MCM-41 based catalyst displays a much higher selectivity for the branched product **13b**, which moreover is formed with a very high enantiomeric excess (Scheme 39):

Scheme 39



C. Hydrosilylation

US-Y-anchored proline-derived chiral ligands (cfr. Scheme 33) were metalated with Rh and applied as catalysts in the hydrosilylation of, e.g., styrene with phenyldimethylsilane.[133−136,152] Obviously, no stereogenic centers are created in such reactions. Very high regioselectivity for the linear addition product was observed.

D. Epoxide Ring Opening

The kinetic resolution of epoxides such as 1,2-epoxyalkanes is a recent, highly performant technology for production of enantiomerically pure epoxides and opening products.[153] In a preferred version of the reaction, water is used in a hydrolytic opening mediated by chiral Cr-salen complexes.[153a] Such complexes have been anchored to aminopropylated MCM-41, either by a coordinative bond, or by a covalent bond starting from a chloromethyl-functionalized Schiff base ligand.[153b] Unfortunately, reported ee's in the opening of 1,2-epoxycyclohexane with trimethylsilyl azide are significantly lower with the heterogenized complex (8−70% ee) than with the homogeneous catalyst (up to 84% ee).

VI. Concluding Remarks

Immobilization of metal ions and metal complexes on inorganic matrices has opened many tracks to more practical fine chemicals processes. A serious caveat is, however, needed regarding the true heterogeneity of several of these new catalytic materials. Particularly physisorption of hydroformylation or even hydrogenation catalysts may in many cases lead to systems with poor stability. On the other hand, as illustrated by the examples, the catalytic properties of the metal center may often benefit from the association with the matrix. Mononuclearization, e.g., by covalent attachment or entrapment, can lead to new reaction pathways or suppression of binuclear deactivation pathways. Modifications of the polarity of the material can increase the reactivity of the embedded center, or can decrease its liability to deactivation. In rare cases, enhanced stereo- or even enantioselectivity have resulted from complex immobilization, via mechanisms related to the "confinement concept". Accurate control of pore shapes and dimensions is needed to precisely control the environment of the active site, and it is clear that for such aims zeolites and ordered mesoporous molecular sieves offer much better perspectives than relatively disordered, amorphous materials such as silica or alumina. In the case of ordered mesoporous materials, there are several illustrations of the effect of pore diameter on the reactions of embedded complexes. However, the influence of other features of these materials, e.g., silanol group density, particle size, preparation method, etc., has been much less documented, and deserves more attention.

Despite the numerous encouraging results, induction of general concepts from the scattered case studies remains risky. It seems that many successful catalysts have resulted from the fortuitous combination of a metal, a ligand, a support and reaction conditions. Chemists in this domain have often worked in actually combinatorial fashion, with numerous failures preceding a good catalytic material. Increased application of combinatorial techniques may in the future therefore contribute to faster developments, with the condition that the creativity of the human mind can keep pace with the speed of experimentation.

VII. References

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