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Journal of Catalysis 216 (2003) 298–312

JOURNAL OF
CATALYSIS

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State of the art and future challenges of zeolites as catalysts

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Received 1 September 2002; revised 18 November 2002; accepted 19 November 2002

Abstract

The control of pore diameter and topology of zeolites, as well as the nature of active sites and adsorption properties, allow in many cases the a priori design of catalysts for applications in the fields of oil refining, petrochemistry, and the production of chemicals and fine chemicals. The potentiality of nanocrystalline, delaminated, or ultralarge pore catalysts and of zeolites formed by channels with different dimensions is outlined.

Keywords: Zeolite; Zeotype; Nanocrystalline; Delaminated and ultralarge pore zeolites; Acid, basic and redox catalysis; Oil refining; Petrochemistry; Chemicals; Fine chemicals

1. Introduction

Zeolites are crystalline silicates and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing channels and cavities of molecular dimensions. Crystalline structures of the zeolite type but with coordinated Si, Al, or P as well as transition metals and many group elements such as B, Ga, Fe, Cr, Ge, Ti, V, Mn, Co, Zn, Be, Cu, etc. can also by synthesized, and they are referred by the generic name of zeotypes; they include, among others, $ALPO_4$, SAPO, MeAPO, and MeAPSO molecular sieves [1–5].

Such tridimensional networks of well-defined micropores can act as reaction channels whose activity and selectivity will be enhanced by introducing active sites. The presence of strong electric fields and controllable adsorption properties within the pores will produce a unique type of catalyst, which by itself can be considered as a catalytic microreactor. Summarizing, zeolites are solid catalysts with the following properties:

- High surface area.
- Molecular dimensions of the pores.
- High adsorption capacity.
- Partitioning of reactant/products.
- Possibility of modulating the electronic properties of the active sites.
- Possibility for preactivating the molecules when in the pores by strong electric fields and molecular confinement.

If the accumulation of knowledge allows us now to see many catalytic possibilities for zeolites, the beginnings in this field were much more limited. Indeed, the two first properties outlined above, i.e., high surface area and molecular dimensions of the pores, were early recognized by Barrer [6,7], who applied them to the separation of linear and branched hydrocarbons. Thus, Union Carbide invested heavily in fundamental research on zeolite synthesis and separation of molecules and the Linde Division developed in 1948 molecular sieve commercial adsorbents based on the synthetic aluminosilicates zeolites A and X [8,9]. Very soon, Rabo and his group at Union Carbide envisaged the possibilities of zeolites as catalysts by introducing acid sites and rationalizing that the interaction between acid sites and reactant molecules involved not only the protic sites but also the adsorption of the molecule onto the surrounding zeolite crystals [10]. These studies opened the door for perhaps the biggest revolution in oil refining, the introduction of acid zeolite Y as a commercial FCC catalyst by Mobil (today ExxonMobil) [11].

The different features of zeolites that make these catalysts unique will be discussed.

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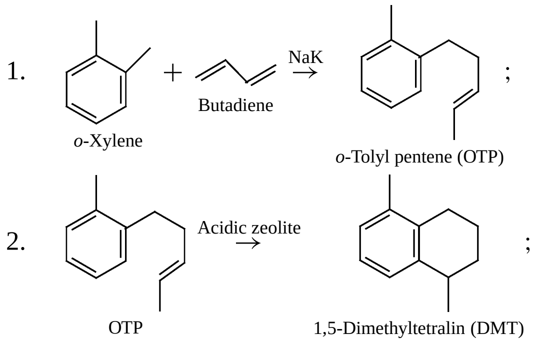
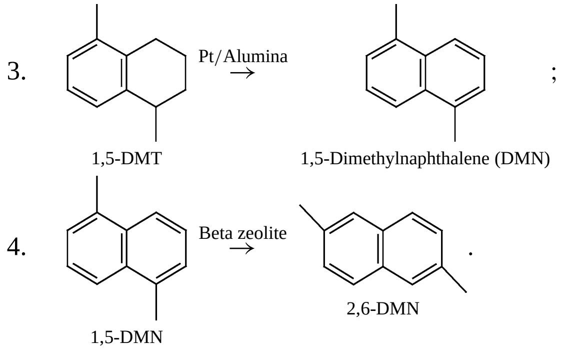
doi:10.1016/S0021-9517(02)00132-X

2. Shape selectivity control

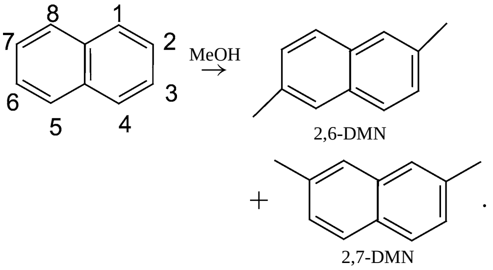
Analogously to enzymes, zeolites with their regular well-defined pore dimensions are able to discriminate [12] reactants and products by size and shape when they present significant differences in diffusivity through a given pore channel system. A particular relevant example of this is the selective cracking of *n*-paraffins and *n*-olefins with respect to their branched isomers using medium-pore-size zeolites with pore diameters in the range 0.45–0.56 nm. This effect is based on zeolite shape selectivity by mass transport discrimination, when the diffusion coefficients for branched and linear hydrocarbons within the pores are at least one order of magnitude different. Researchers from Mobil pioneered extensive research effort on the synthesis of new zeolites and their geometrical implications for reactivity [13,14] that culminated in a series of industrial processes. Among them we can point out the use of ZSM-5 zeolite as an FCC cracking additive that selectively cracked linear versus branched olefins in the gasoline range, producing gasoline with a higher octane number and higher yield of propylene in the gas products. The shape selectivity effect of medium and small-pore zeolites for hydrocracking paraffins has been industrially applied in the selectoforming and catalytic dewaxing processes. More recently, researchers from Chevron [15] have shown that medium-pore zeolites with unidimensional channel systems (the author worked with SAPO-11) can be used to produce selectively monobranched versus multibranched isomers during the hydroisomerization of long chain *n*-paraffins. This was the origin of the isodewaxing process [16]. An explanation for this effect has been based on the diffusivity differences between linear, monobranched, and dibranched products and assuming that the branching reaction occurs in the pore mouth [17]. However, recent theoretical and experimental work [18–20] have challenged this hypothesis and they explain the selective isodewaxing process by geometrical restrictions within the channels to form the transition states of the dibranched isomers.

Reaction product discrimination by mass transport effects can also occur in zeolites, and sometimes practical advantage is taken on this. For instance, the BP-AMOCO process for the synthesis of 2,6-dialkylnaphthalene, a product useful as a polymer intermediate, is carried out in four different steps that require four different reactors:



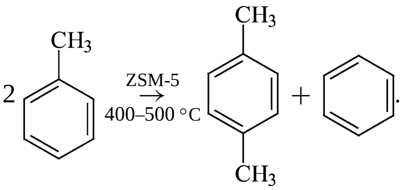


It is clear that the process could be simplified if a selective catalytic dialkylation of naphthalene by methanol or propylene could be carried out:



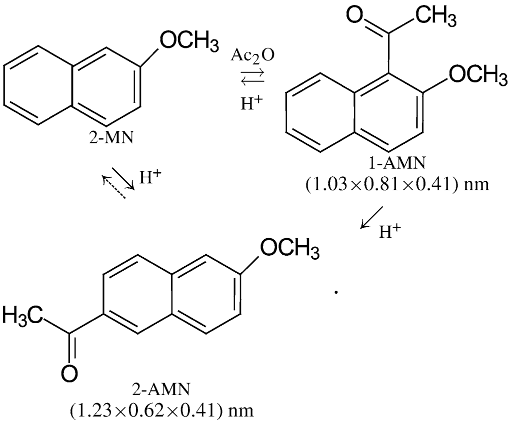
Large-pore zeolites should be adequate for producing this reaction, and USY, Beta, and Mordenite are able to alkylate naphthalene with isopropanol with good selectivities to the 2, 6 isomer, while producing far less tri- and polyalkylated products than with a nonmicroporous fluorinated resin [21]. Horsley et al. [22] have shown by molecular mechanics that a unidirectional 12-member ring zeolite such as Mordenite (0.64 × 0.70 nm) presents a significant energy barrier to diffusion of the 2,7-DMN isomer, while diffusion of 2,6-DMN was not impeded. However, when a unidirectional 12-member ring zeolite with larger pore diameter (0.72 nm) was considered (zeolite L), no significant energy barrier was found. Differences in the diffusion coefficients of the two isomers were considered by ENICHEM researchers for selecting MTW zeolite for the selective alkylation of naphthalene with methanol [23].

Differences in the rate of product diffusion also occur and are further enhanced during the industrial process for producing dimethylbenzenes [24] (preferably *p*-xylene) by selective toluene disproportionation using the medium-pore ZSM-5 zeolite:



p-Xylene selectivities of $\geqslant 80\%$ are obtained by a controlled interplay of intrinsic chemical kinetics and transport discrimination of products. In an unmodified ZSM-5 zeolite the kinetics of the two reactions prevail, and due to the much faster rate of isomerization ($K_{\mathrm{isom}}/K_{\mathrm{disp}} \approx 5000$) the thermodynamic equilibrium of the three dimethylbenzene isomers is produced. However, by taking into account the critical diameter of *p*- and *o*-xylene, introducing diffusional restrictions using larger crystallite sizes, and treating the catalyst with phosphorus, coke, or other modifiers that block pore entrances and increase tortuosity in the xylene diffusion path, Olson and Haag [25] achieved $K_{\mathrm{isom}}/K_{\mathrm{dis}} \leqslant 1$, leading to an extraordinary enhancement in *p*-xylene selectivity.

A final example where differences in product diffusion rates have been used to increase selectivity toward the desired product is the acylation of 2-methoxynaphthalene with acetic anhydride to produce 2-acylmethoxynaphthalene, which is an intermediate for the synthesis of the anti-inflammatory Naproxen:



The differences in size between the two acylated isomers indicate that selectivity can be influenced by using zeolites as catalysts if the bulkier product cannot be formed inside the channels and the external crystallite surface is passivated or, even if the bulkier product is formed inside, its diffusion out to the reaction media will be much slower. In this case, the consecutive reaction shown in the above scheme will occur in a proportionally larger extension, increasing the selectivity to the desired 2-AMN product. The first effect was shown using Beta zeolite as catalyst. This zeolite, having two channels of 0.72 × 0.62 nm and one of 0.55 nm pore diameter can achieve a selectivity of 48% to 2-AMN for a conversion level of 39% [26]. Further improvement in selectivity was achieved by first increasing the zeolite crystal size to 9 µm (60% selectivity), and also when the external surface was silylated (92% selectivity). However, conversion dropped with silylation from 48 to 8%.

In an attempt to increase selectivity, others [27] have used surface dealuminated nanocrystallites of Beta zeolite with a conversion of 31% and selectivity close to 80%.

A further tuning of zeolite pore diameter for the above reaction can be achieved using two other 12-member ring tridirectional zeolites named ITQ-7 and ITQ-17 with pores of 0.62 × 0.61 (2)–0.63 × 0.61 (1) nm and 0.62 × 0.66 (2)–0.63 × 0.63 (1) nm, respectively. For these two zeolites selectivities to 2-AMN were 64 and 70% for conversion levels of 40 and 68% [28], respectively, which are still far from optimum. It appears then to us that it will be difficult to further improve the selectivity to the desired 2-AMN isomer, at high levels of conversion, by using zeolite's shape selectivity. It is probably a better solution to this problem to find a very active nonzeolitic catalyst for the transformation of 1-AMN into 2-AMN.

When the catalytic reaction occurs inside the zeolite pores, the size and shape of channels and cavities can be used, in some cases, to select the desired reaction pathway by making use of the so-called "transition state shape selectivity" [29–32]. This occurs when the special configuration around a transition state located in the crystalline volume is such that only certain configurations are possible.

It appears to us that transition state shape selectivity effects can be more limited in zeolites than in enzymes owing to the rigid structure of the zeolite. However, we also believe that their possibilities can be enhanced by adequate control of internal defects and the introduction of multicenters within the framework. These will enlarge the possibilities of selecting a given transition state via geometry plus chemical interactions [33].

3. Control of adsorption properties

Enzymes are also able to select reactants and products by polarity and in other cases can perform bimolecular reactions between two reactants with different polarities. It should also be emphasized that enzymes are able to work in aqueous media but the adsorption of water can be controlled. Thus, using the enzymatic model, the possibilities of zeolites as catalysts could be improved if the adsorption properties could be adjusted by either selecting an adequate solvent or, even better, controlling the hydrophobicity–hydrophilicity of the solid. We will briefly discuss this below.

Zeolites containing charges are normally hydrophilic materials that, depending on the number of charges (extraframework cations and framework Si/Al ratio), can be more or less selective adsorbents for polar or nonpolar molecules. However, pure silica zeolites with no positive charges are highly hydrophobic materials, provided that the number of internal silanol defects is low. It is then clear that the polarity of a given zeolite could be controlled by controlling the Si/Al ratio by direct synthesis or by postsynthesis treatments, and this, together with appropriate control of the number of silanol groups by synthesis or postsynthesis treatments, should make it possible to prepare zeolite catalysts within a wide range of surface polarities. An adsorption-based methodology for measuring zeolite hydrophobicities has been developed by Weitkamp et al. [34].

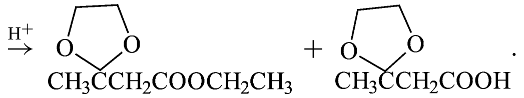
The effect of surface hydrophobicity on catalyst performance was observed by Namba et al. [35] during the direct esterification of acetic acid with *n*-, iso-, and *tert*-butyl alcohol on different zeolites. These authors observed that the water formed poisoned the acid sites of the catalysts. However, the poisoning was lower with the more hydrophobic high-Si/Al-ratio ZSM-5 catalysts, which were more active despite having a smaller number of acid sites. Ogawa et al. [36] explored the hydrolysis of water-insoluble esters with a high Si/Al ratio ZSM-5 that was made more hydrophobic by silylation with octadecyltrichlorosilane. The ester in toluene was contacted with H_2O for reaction. The hydrophobic zeolite allowed the reaction to occur in the two-phase system with good activity.

Recently, we have shown that it is possible to prepare either highly hydrophilic Beta zeolites that preferentially adsorb H_2O and polar reactants versus nonpolar hydrocarbons, or very hydrophobic Beta zeolites able to adsorb 150 times more *n*-hexane than water [37–39]. Highly hydrophobic Beta zeolites could be obtained by synthesizing in fluoride media high-Si/Al-ratio samples that are free of defects.

By achieving the two extremes, samples with intermediate hydrophobicities can readily be prepared. These Beta samples with controlled polarity give good activity and selectivity for producing alkylglucoside surfactants by reacting glucose and fatty alcohols. In this case glucose is a highly hydrophilic reactant, while the fatty alcohols are much more hydrophobic. Then, when a regular hydrophilic zeolite is used, glucose is preferentially absorbed, competing very favorably with the alcohol for the acid sites, and slowing the reaction. In this case, a more hydrophobic defect-free Beta zeolite with a Si/Al ratio of ∼ 100 is a much better catalyst than other Beta samples with a larger number of acid sites (lower Si/Al ratio) or with more structural defects [40].

This principle has also been used for the synthesis of the Fructone (ethyl 3,3-ethylendioxybutyrate) fragrance at pilot plant levels:

$CH_3COCH_2COOCH_2CH_3 + HOCH_2CH_2OH$



In this example, there is also a difference in polarity between the two reactants, and the catalytic results presented in Fig. 1 [41] show that using either Y or Beta zeolites an optimum between amount of active site and hydrophobicity of the zeolite should be achieved.

We will present later that the control of the adsorption properties is vital when the selective oxidation of hydrocarbons is performed with metal-containing zeolites using aqueous H_2O_2 as oxidant.

4. Activating the reactants by confinement effects in zeolites

When a molecule is confined in the pores of a zeolite, the sorption energy will include different energy terms

$$E = E_D + E_R + E_P + E_N + E_Q + E_I + E_{AB},$$

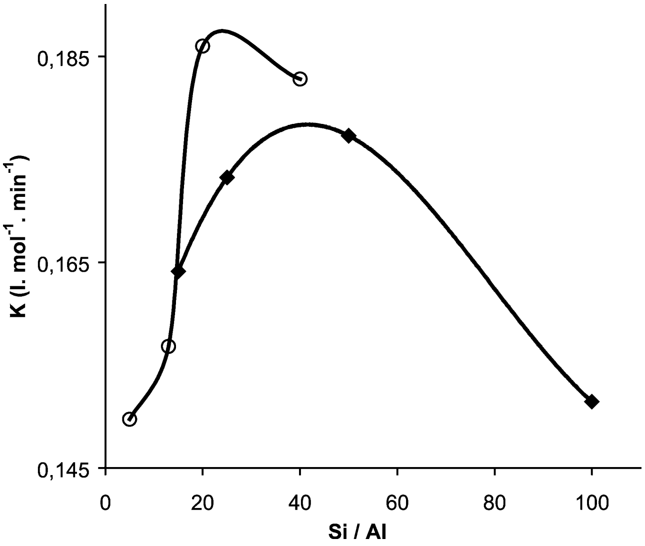


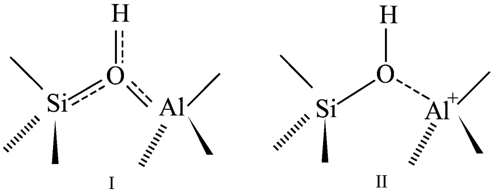
Fig. 1. Second-order kinetic rate constant (K) of USY (○) and Hβ (◆) zeolites with different Si/Al ratios at 1 h, when the reaction was carried out at 419 K; catalyst amount, 7.4% wt/wt (of ethylacetoacetate amount); volume ratio toluene/ethylacetoacetate = 26.6.

where E_D and E_R are the attractive and repulsive contribution terms, respectively, from the van der Waals interaction; E_P, E_N, and E_Q are the polar, field-dipole, and field gradient-quadrupole terms, respectively; E_I is the sorbate–sorbate intermolecular interaction energy, and E_{AB} is the energy of the intrinsic acid–base chemical interaction. One can safely assume that the interaction in the confined space of the pores will be characterized by the geometry of the environment of the active site (E_D and E_R) and by the chemical composition of the environment (E_P and E_N). Derouane [42] has proposed that owing to the confinement effect, the sorbate molecules in zeolites tend to optimize their van der Waals interactions with the zeolite walls. This effect differentiates zeolites with amorphous materials and makes them more similar to enzymes in the sense that confinement effects may lead to site recognition or molecular pre-organization of specific sites of sorbate reactants and reaction intermediates or products [43,44]. When the size of a guest molecule approaches the size of the pores and cavities of the zeolite, one must also consider electronic confinement, which can strongly influence the energetic situation of the reactant, changing its reactivity. This electronic confinement implies that owing to the partial covalent character of the zeolite, electrons are not localized on the framework atoms, but are partially delocalized through the bulk. Thus when the size of the zeolite channels approaches the size of the confined molecule, the density of the most external molecular orbital (HOMO) will drop suddenly to nearly zero when reaching the walls. This will produce a contraction of the orbitals of the guest molecule with corresponding changes in the energy level and preactivation state. This effect was determined by theoretical calculations made with a molecule of ethylene confined into a microscopic cavity [45]. Experimental evidence of electronic confinement was presented by Marquez et al. [46]. These authors have studied the photophysical properties of naphthalene within pure silica zeolites of different pore diameters by diffuse reflectance, steady-state, and time-resolved emission spectroscopy, fluorescence polarization, and FT Raman spectroscopy. The results showed that the naphthalene molecule was strongly affected by the zeolite host. Distortion is reflected in the bathochromic shift of the 0–0 transition, the shortening of the fluorescent lifetimes, the observation of vibronic couplings, the appearance of room-temperature phosphorescence, and the shift of the Raman peaks to lower vibration energy due to the weakening of the naphthalene bonds. The electronic structure of naphthalene within different zeolites was computed on periodic models by using Hartree–Fock and Kohn–Sham theories. The naphthalene π electrons are affected by the confinement effect. It appears to us that because of the electronic confinement, the "basicity" of an adsorbed molecule should be higher than when it is in the gas phase. If this is so, its reactivity toward the acid sites should be larger. This may also explain why zeolites show stronger acidities than expected when probe molecules are used to determine the acidity. The effects of zeolite confinement on the reactivity of adsorbed molecules has been proved to be significant in photochemical reactions in zeolites [47].

5. Catalytic acid sites in zeolites

To summarize all the relevant work done in this field in a few pages has become an impossible task for us. Nevertheless, we will try to emphasize some published work that illustrates the possibilities of zeolites as acid catalysts.

Brønsted acid sites are generated on the surfaces of zeolites when Si^{4+} is isomorphically replaced by a trivalent metal cation such as, for instance, Al^{3+}. This substitution creates a negative charge in the lattice that can be compensated by a proton. From a structural point of view, the Brønsted acid site in a zeolite can be seen as a resonance hybrid of structures I and II,



where structure I is a fully bridged oxygen with a weakly bonded proton, and structure II is a silanol group with a weak Lewis acid interaction of the hydroxyl oxygen with an Al. Based on Gutmann's rules to explain the interaction between atoms giving and accepting electron pairs [48], Mortier [49] proposed a general theory that could explain why model I could be more representative of the situation of the acid site in a crystalline zeolite structure, while model II would represent the situation in an amorphous silica–alumina where no stabilization by long-range symmetry exists [50].

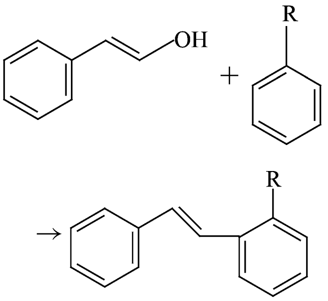
A large number of physicochemical techniques have demonstrated the presence of those Brønsted acid sites on zeolites upon dehydration [51–62].

Theoretical calculations and modeling studies of zeolites have been done using ab initio calculations that attempt to predict quantitative results of experimental zeolite properties. These use model clusters, embedded model clusters, and periodic systems to mimic zeolite structures with increasing range of interaction from short to medium and long range. For illustrative reviews on the subject see [63–69].

From the zeolite acid catalyst design point of view, it is clear that the total number of Brønsted sites is, in principle, directly related to the total number of framework T^{III} atoms present [70]. However, in the case of high-aluminum-content samples not all the acid sites have the same acid strength, and this changes with the number of aluminum atoms in the next nearest neighbor position (NNN) of the aluminum atom which supports the acid site [71].

A completely isolated Al tetrahedron will have zero NNN and supports the strongest type of framework Brønsted acid site. Barthomeuf [72] extended this idea by using topological densities to include the effects of layers one through five surrounding the Al atom. Both the Al NNN and the topological density theory predict that by changing the framework Si/Al ratio, either by synthesis or by postchemical synthesis, it is possible to change not only the total number but also the electronic density on the bridging hydroxyl group, and therefore to change the acid strength of the Brønsted acid site. Thus, when reactions demanding low acidities are to be catalyzed, zeolites with lower framework Si/Al ratios will be preferred. In contrast, when strong acidities are required, zeolites with isolated framework Al (Si/Al ratios $\geqslant$ 9–10) will be chosen.

The acid strength of the Brønsted acid sites can also be modulated through isomorphic substitution, either by synthesis or by postsynthesis methods, of Si for trivalent atoms other than Al. For instance, the Ga-substituted zeolites gave stronger acid sites than boron and weaker than Al-substituted zeolites. The fine tuning of acid strength is a very interesting property of zeolites in catalysis and is of paramount importance for controlling reaction selectivity. For instance, in the alkylation of benzene and toluene with a bifunctional alkylating agent (cinnamyl alcohol):



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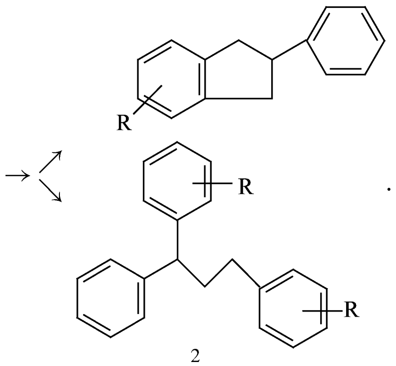

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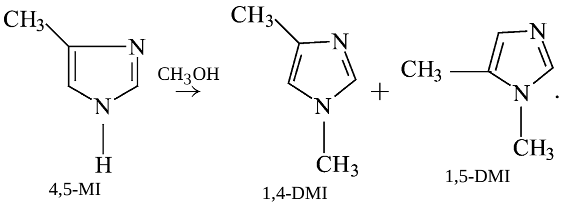
High regioselectivity with respect to the allylic system for the desired intermediate **1** is obtained with a HY zeolite with weak acidities (low Si/Al ratio and partial $Na^+ \rightarrow H^+$ exchange). Stronger acidities lead to further condensation and larger amounts of 1,1,3-thriphenylpropane **2** that not only decrease selectivity but also deactivate the catalyst [73]. In another example, when high-purity isobutene has to be obtained for the production of isobutene copolymers, a very selective mildly acidic catalyst is required which can decompose MTBE to isobutene and methanol without giving consecutive reactions. In this case, Snamprogetti uses B-ZSM-5 to selectively catalyze the reaction. A zeolite catalyst with weak acid sites such as B-ZSM-5 containing Ce is active and selective for the isomerization of 2-alkylacroleines into 2-methyl-2-alkenals without performing skeleton isomerization [74]. Ono has discussed zeolites as solid acids [58] and has also shown the influence of the acid strength on the regiospecific methylation of 4(5)-methylimidazal (4,(5)-MI) to 1,4- and 1,5-dimethyl imidazol (1,4-DMI and 1,5-DMI):



Thus, using zeolites HY and H Beta, both having large pores, but with different acid strengths the ratio 1,4-DMI/1,5-DMI can be changed from 0.29 to 2.0 with DMI yields of 100 and 50%, respectively.

The control of zeolite acidity is of special importance in catalyzing reactions involving strong bases such as NH_3 or pyridines. In these cases a zeolite catalyst with too strong acidity should be rapidly poisoned by the adsorption of the basic reactant or product. This is for instance the case for the aldol condensation of aldehydes and ketones with ammonia, for the production of pyridine and 3-methylpyridine, which are intermediates in the synthesis of vitamin B3. In this case a ZSM-5 zeolite with milder acidity achieved by doping with Th, Co, or Pb is the active catalyst [75].

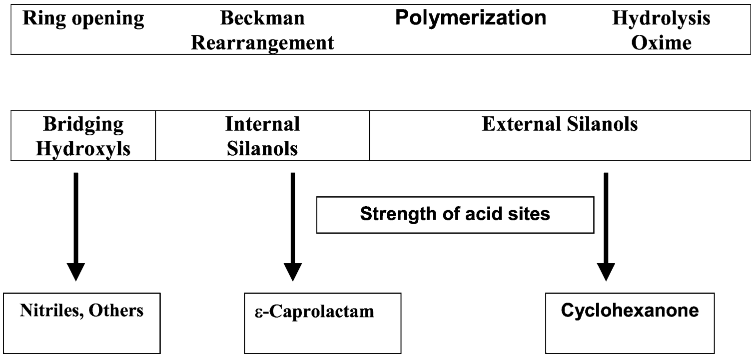
Finally, there is an extremely interesting case where, contrary to a primary prediction, the use of the very weakly acid internal silanols of ZSM-5 zeolite has lead to an important commercial process such as the production of ε-caprolactam by the Beckmann rearrangement of cyclohexanone oxime [76,77].

In this process, cyclohexanone oxime is vaporized and fed into a fluidized-bed-type reactor with methanol vapor. There, a catalyst mainly composed of high-silica MFI zeolite is loaded, while MFI containing stronger acid sites with bridging hydroxyl groups gives undesired nitriles and catalyst deactivation precursors. It is interesting to see that the less active internal silanols of either ZSM-5 [78] or Beta zeolite [27] are more selective and allow longer use of the catalyst (Scheme 1).

The control of acid strength as well as the density of acid sites of zeolite catalysts has also led to successful catalysts and processes in the field of oil refining and petrochemistry. For instance, in the isomerization of ethylbenzene to xylenes the reaction involves, as the first step, partial hydrogenation of the aromatic ring. This is followed by ring expansion and contraction to yield xylenes. While the first step is catalyzed by Pt metal, the ring expansion and contraction is an acid-catalyzed reaction that occurs on mordenite zeolite. However, if the strong Brønsted acid sites of the protonic form of mordenite are present, the cracking of partially hydrogenated ethylbenzene also occurs in a large extension. Then, moderating the acid strength by partial exchange of acid sites with alkaline or, even better, with alkaline earth cations produces higher selectivity to xylenes [79–81]. There is an intriguing effect of acid strength in driving the isomerization of xylenes through either a unimolecular or a bimolecular mechanism. It has been shown that zeolites containing strong acid sites produce mainly unimolecular isomerization, while mesoporous molecular sieves with weaker acid sites catalyze the reactions through a bimolecular intermolecular process [82].

Sometimes, the acid site density is even more important than acid strength. This has an important impact on adsorption properties and therefore can be used to control selectivity when uni- and bimolecular reactions compete. Then, zeolites with a low density of Brønsted sites (low density of framework T^{III} cations or high T^{IV}/T^{III} ratios) will favor unimolecular reactions. On the other hand, high density of T^{III} atoms will favor bimolecular reactions by increasing the adsorption of reactants. This factor is being used together with the control of pore dimensions to regulate the ratio of xylene isomerization (unimolecular) versus xylene disproportionation to toluene and trimethylbenzenes (bimolecular).

In the case of fluid catalytic cracking (FCC), besides hydrocarbon cracking, hydrogen transfer between olefins and saturated molecules occurs. The ratio of rates for cracking (uni- and bimolecular) and hydrogen transfer (bimolecular) has important implications for the final yield of olefins and aromatics, and consequently for gasoline octane number, propylene yield, and coke formation. Thus, when high yields of olefins are to be obtained, higher ratios of cracking



Scheme 1.

to hydrogen transfer should occur and USY zeolites with low framework Al content are preferred.

6. Future perspectives in zeolite acid catalysts

We believe that one has to look at acid zeolites from the point not only of view of their intrinsic acidities, but the role played by the short- and medium-long range effects on adsorption and stabilization of the activated complex should also be considered. It seems logical that the structure will determine the spatial conformation as well as the number of hydrogen bonds that the “protonated transition complex” can form with the framework anion in order to get the minimum energy configuration. As occurs in the case of enzymes, this hydrogen bond-acceptor ability can be an important feature of zeolites as micro- or nanocatalytic reactors. If this is so, it is evident, at least to us, that it is not sufficient from a reactivity point of view to consider the global framework Si/Al ratio; the distribution of T^{III} atoms in the different framework positions should also be taken into account. Notice that a random distribution of T^{III} atoms will not necessarily occur in all synthesized or post-synthesis treated zeolites [83]. Thus, the presence of the active site in different geometrical positions can stabilize the reaction transition complex differently.

Finally, it would be interesting for some demanding processes (short-chain paraffin isomerization, cracking, alkylation, etc.) to have zeolites with very strong acid sites that could allow some processes to be carried out at lower reaction temperatures or with smaller catalyst inventories. This can, however, be difficult since a very high acidity could not be taken by the zeolite framework which would become then hydrolyzed. Nevertheless, it would be interesting to think how we may generate structures and compositions that allow a higher delocalization of the negative charge, leading to higher acidities. Efforts toward achieving stronger acid sites in zeolites, but in an indirect way, have been made by preparing organic-functionalized zeolites by direct synthesis, where more acidic sulpfonic groups can be produced [84].

7. Zeolites with basic active sites

It is also possible to generate basic sites within the pores of zeolites and in this way to take advantage of the properties of zeolites in base catalysis. In the case of zeolites the basic sites are of Lewis type and correspond to framework oxygens, and the basicity of a given oxygen will be related to the density of negative charge. Taking this into account, the basicity will be a function of framework composition, the nature of extraframework cations, and the zeolite structure. Quantitatively, the average charge on the oxygens and the changes with framework composition can be known by calculating the average Sanderson electronegativity (ASE) of the zeolite [85,86].

In agreement with this, a good correlation between the average basicities calculated by ASE and catalytic activity for side chain alkylation of toluene with methanol and Knoevenagel condensation of benzaldehyde with different compensating cations and framework compositions has been found [87]. The above correlation has also been observed by using probe molecules such as, for instance, pyrrole, acetylenes, and chloroform combined with FTIR and NMR spectroscopies [88–92]. Methoxy groups formed from methyl iodide and bounded at framework oxygens of alkali-exchanged zeolites Y and X have also shown, by ^{13}C MAS NMR spectroscopy, a correlation between the isotropic chemical shift of those surface methoxy groups and the ASE [93,94].

Calculation of charges on selected oxygen atoms [95] shows that in the case of faujasite this changes from oxygen to oxygen when the compensating cations are Na, K, Rb, or Cs. This charge increases for oxygens O2 and O3 while it decreases for O1 and O4 on passing from Na to Cs [96]. Further information on basicity of zeolites can be found in some excellent reviews [97–99]. The basicity of alkaline-exchanged zeolites is relatively weak and it is possible to abstract protons in organic molecules with pK_a of 10.7 [100]. However, when Si is partially replaced by Ge the basicity of the framework oxygens increases, and they can abstract protons from organic molecules with pK_a of 11.3 [101].

Interesting work on the catalytic activity of alkaline-exchanged faujasites has been reported by Ono [102], where phenylacetonitrile is selectively monomethylated by methanol and dimethylcarbonate. The order of basicity found was CsX > RbX > NaX > LiX, with CsX > CsY.

Other reactions such as Knoevenagel, aldol and Claisen–Schmidt condensations that do not require strong basicities are also successfully catalyzed by alkaline zeolites [103–105].

An interesting feature of basic zeolites is that they are useful catalysts for some reactions that require acid–base pairs. In this situation, the Lewis acidity of the cation and the basicity of the oxygen should be balanced. Reactions such as toluene chain methylation or selective N-alkylation of N-methylaniline, benefit from the presence of tunable acid–base pairs in alkaline-substituted zeolites [106–115].

In an attempt to profit from the microporosity of zeolites, while increasing basicity, framework oxygen atoms may be partially replaced by nitrogens. This was attempted as early as 1968 by treating a Y zeolite with NH_3 at high temperature, and the authors claimed that SiO_3 (NH_2) groups were produced [116]. Unfortunately, the basicities of the materials were not measured.

Stronger basicities have been achieved by generating extraframework imides within zeolite Y channels by immersing the alkali-exchanged zeolite in a solution of metallic Na, Yb, or Eu in liquid ammonia. After the solvent was removed by evacuation and heated in vacuum at ~ 450 K a basic catalyst was obtained [117].

Strong basic sites have been created by forming Na^0 clusters in supercages of Y zeolite and on the external surface [118–120] and by forming alkali or alkaline earth oxide clusters [121–124].

8. Future trends on basic catalysis in zeolites

By generating framework and/or extraframework basic sites, it is now possible to prepare zeolites within a very large spectrum of basicities. Then, depending on the reaction to be catalyzed, it should be possible to select the most adequate basic zeolite from the very mild alkaline-exchanged zeolites up to very strong alkali- or alkaline-oxide-cluster containing zeolites. In principle, basic zeolite catalysts should be available for any of the following base-catalyzed reactions: olefin double-bond isomerization; hydrogenation of olefins, alkynes, and aromatics; side-chain alkylation of alkylaromatics with olefins; aldol condensation of acetone; O-alkylation of phenols; Knoevenagel and Claisen–Schmidt condensations; Tishchenko and Wittig–Horner reactions; aromatization of cyclodienes; production of allyl alcohols from alkenes; dehydrogenation of alkylamines to nitriles; synthesis of primary mercaptans from alcohols and H_2S; formation of thiophene or pyrrole by reacting furan with H_2S or NH_3, respectively; and reductive decyanation of nitriles.

Some of the above reactions have been worked with zeolites, but most of them, which are also of commercial interest, remain to be explored. We should rely on the imagination of researchers to better exploit a relatively unexplored subject such as the combination of basicity and shape selectivity of zeolites to prepare new chemicals. Combining this with improved work-up procedures and/or catalyst resistance to H_2O and CO_2 will open new possibilities for basic zeolites.

9. Zeolites with redox active sites

Many oxidation processes in the liquid phase are catalyzed by soluble oxometalic compounds. These catalysts present two main limitations. One is the tendency of some oxometalic species to oligomerize, forming μ-oxocomplexes that are catalytically inactive. Another limitation is the oxidative destruction of the ligands that lead to the destruction of the catalysts. Solving these two problems will require isolating the catalytically active sites on inorganic matrices through supporting metals, metallic ions, metal complexes, and metal oxides, or synthesizing molecular sieves where the oxidating atom is incorporated into the framework. Again, this last type of catalysts require many features encountered in oxidation enzymes: isolated and identical stable sites, in an environment adequate from the point of view of adsorption and geometry. Zeolites with their pores and cavities can introduce steric effects, while metal atoms incorporated into the framework may, in some cases, be stable toward leaching. If all these characteristics are important for a successful heterogeneous solid catalyst working in the liquid phase, what really makes the redox molecular sieve catalysts unique is their adsorption properties, which can be tuned from the point of view of hydrophobicity–hydrophilicity. This should allow these catalysts to add an extra activity–selectivity property by selecting the proportion of reactants with different polarities which will be adsorbed into the pores. This is particularly important when organic compounds have to be oxidized using aqueous H_2O_2.

With all the above desired characteristics in mind, researchers at ENI succeeded in introducing, by direct synthesis, Ti into the framework of silicalite, producing a TS-1 redox molecular sieve oxidation catalyst [125–127].

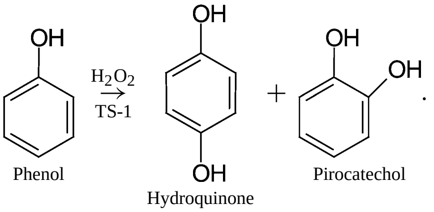
TS-1 has an MFI structure formed by a tridimensional system of channels with 0.53×0.56 nm and 0.51×0.51 nm, where the incorporation of Ti into the framework has been demonstrated by a series of spectroscopic techniques including XRD, UV–visible, XPS, and EXAFS–XANES [128]. More recently, electrochemical and photochemical techniques have also been successfully used not only to elucidate the coordination of Ti, but even to discuss on Ti in different “T” positions [129,130]. By means of these techniques it has been proven that in well-prepared TS-1 catalysts Ti is present in tetrahedral coordination, preferentially as isolated Ti(IV) atoms. Owing to the silica framework with a small

Table 1
Influence of Al content and zeolite polarity on activity and selectivity of Ti-Beta for epoxidation of 1-hexene with H_2O_2 using methanol as a solvent

Zeolite characteristics	Chemical composition		TOF	Epoxide selectivity
	Si/Al ratio	TiO_2 (wt%)	(mol/mol Ti h)	(%)
Framework Al + defects	300	4.7	20.8	25.9
No aluminum but defects present	∞	2.5	28.6	75.4
No aluminum, no defects (F^- synthesis)	∞	2.5	32.2	96.4

number of defects, the TS-1 is a hydrophobic material and thus can use H_2O_2 as oxidant in a large number of reactions. Among them, we can highlight the following: epoxidation of linear olefins, oxidation of linear alkanes to alcohols and ketones, oxidation of alcohols, hydroxylation of aromatics, oxidation of amines, and oxidation of sulfur compounds and ethers [131–138].

As was shown before for acid-catalyzed reactions, shape selectivity effects can also be important with redox zeolites. For instance, in the case of the hydroxylation of phenol the shape selective properties of the structure are desirable when hydroquinone is the most desired product:

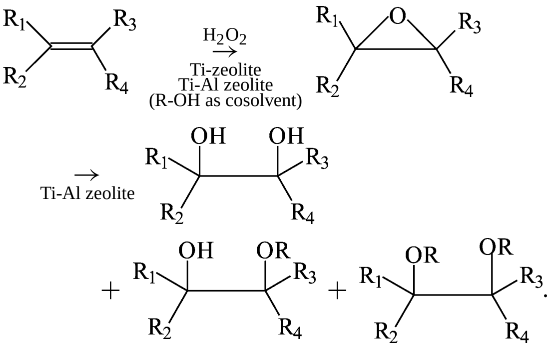


The smaller kinetic diameter of hydroquinone than of pirocatechol would recommend maximizing the molecular sieve effect of the TS-1 by preparing large zeolite crystals. However, a compromise should be reached in this case, since globally fast diffusion of the diphenols out of the pores is required in order to avoid secondary reactions leading to further oxidated products, tars, and H_2O_2 decomposition. Since it is mandatory to minimize the above negative effects, crystal sizes as small as possible are preferred, and if possible with a deactivated external surface. Small zeolite crystals are also desired for propylene epoxidation, since larger crystals deactivate faster because formation of bulky secondary products may partially block the pores.

For commercial uses, TS-1 should be incorporated into a silica matrix in order to deal with the small crystallites and the low attrition resistance of the pure zeolite.

For other reactions where the reactants or products are too large to diffuse through the pores of the MFI and MEL (TS-2) [139] zeolite structures, TS-1 and TS-2 oxidation catalysts become limited [140]. Owing to this, large-pore Ti-zeolites have been synthesized. Among them, the incorporation of Ti by direct synthesis has been demonstrated for BEA (Ti-Beta), MTW (Ti-ZSM-12), ISV (Ti-ITQ), and MWW (Ti-MCM-22) [141–147].

When hydrocarbons are oxidized with aqueous H_2O_2, two phases are formed unless a nonreactive cosolvent is added. Nevertheless, both polar and apolar reactants have to diffuse and adsorb into the pores of the zeolite. It appears that again the polarity of the zeolite plays an important role on the catalyst properties. As was said before, zeolite polarity will increase when increasing the charges present (increasing T^{III} framework atoms) and if defects (internal silanols) are present. In some cases, such as the epoxidation of olefins, the presence of T^{III} atoms, especially if they are compensated by protons, may have a deleterious effect on selectivity by further reacting with the products. This is especially true for epoxides, which in the presence of water hydrolyze to give the corresponding diols and/or ethers:



A very illustrative example for how polarity and acidity influence activity and selectivity during oxidation of olefins is given in Tables 1 and 2 [148].

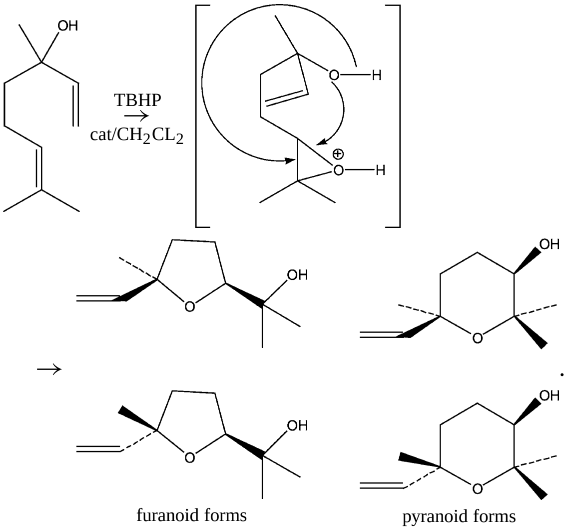
It is evident that the adsorption properties (hydrophobicity–hydrophilicity) of Ti-zeolites are of paramount importance for dealing with reactants with different polarities. Thus, it can also be expected that the polarity and protic–aprotic character of the solvent used will have a strong influence on reactivity. In this sense, it has been found that while methanol is the most adequate solvent for TS-1, acetronitrile is best for Ti-Beta, giving high conversion and selectivity to epoxides [149]. For further inside into reactivity of Ti-zeolites see [150–158].

Table 2
Influence of solvent in allyl alcohol epoxidation with H_2O_2 over TS-1 at 60 °C, and reaction time 8 h

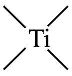
Solvent	Conv. (wt%)	Product selectivity (wt%)		
		Epoxide	Aldehyde	Others[a]
Acetone	96.0	96.0	4.0	–
Acetonitrile	95.0	95.0	5.0	–
Methanol	58.0	82.0	–	18.0
Ethanol	58.0	86.0	–	14.0

[a] Cleavage products of epoxide through alcoholysis and other high b.p. products.

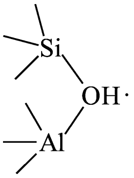
Let us now show how a redox zeolite can be designed to give the same products as an enzyme. Linalool is oxidized by an epoxidase enzyme to give furans and pyrans with high selectivities [159]:



The enzyme has two active sites, an oxidation center that epoxidizes the double bond, and an acid center that opens the epoxide and produces the cyclation and ring formation. We have tried to mimic this by synthesizing a Ti–Al-Beta that will have in the structure both the oxidation site



and the acid site



With this zeolite and using TBHP as oxidant high conversions of linalool with practically 100% selectivity to furans and pyrans were obtained [159].

Besides Ti-zeolites, other transition-metal-substituted zeolites have been synthesized and are also active and selective for carrying out oxidations in liquid phase using H_2O_2 or organic peroxides as oxidants. For instance, V-MEL and V-MFI silicalites have shown activity and selectivity for alkane oxidation and phenol hydroxylation with H_2O_2 [160]. VAPO-5 selectively catalyzes the epoxidation of allyclic alcohols and benzylic oxidations with TBHP [161]. Attention has to be paid to the leaching of vanadium under liquid-phase oxidation, since the homogeneous reaction occurring with the solubilized V can mask the results from the solid catalyst [162].

In the case of Cr-substituted molecular sieves, H_2O_2 may lead to the leaching of some Cr in solution [163]. CoAPO's have also been used for liquid-phase oxidations of alkanes and alkylaromatics. Under these conditions, Co may leach in basic media, in the presence of organic acids, or in the presence of strong polar solvents [164].

Table 3
Mild oxidations with H_2O_2 over isomorphously-substituted molecular sieves

Catalyst	Reactant	Temp. (°C)	Major products
V-ZSM-5	Allyl alcohol	60	Acrolein
V-ZSM-5	Acrolein	60	Acrylic acid
V-ZSM-48	Phenol	80	Catechol, hydroquinone
Sn-ZSM-12	Phenol	80	Catechol, hydroquinone
Sn-ZSM-11	Phenol	75	Catechol, hydroquinone
Sn-ZSM-11	Toluene	80	Benzaldehyde
Cr-APO-5	Ethylbenzene	80	Acetophenone

Sn-silicalite, Sn-ZSM-12, Sn-AlBeta, and dealuminated Sn-AlBeta are active for hydroxylation of phenol, toluene, *m*-cresol, *m*-xylene, naphthalene, and 1,3,5-trimethylbenzene [165,166].

A summary of various reactions on various metal-substituted molecular sieves is given in Table 3 [167].

Special mention should be made of Al-free Sn-Beta for the Baeyer–Villiger (BV) oxidation of cyclic ketones with diluted H_2O_2. This catalyst gives good activity and very high selectivity to the corresponding lactone [168]. When a double bond is also present in the reactant cyclic ketone, a very high chemoselectivity for the BV reaction is observed with the Sn-Beta catalyst (Table 4) [169].

The active site is the framework Sn, which acts as a Lewis acid site. By carrying out a mechanistic study using methylcyclohexanone labeled with ^{18}O as reactant, it was concluded that the BV oxidation with H_2O_2 on Sn-Beta proceeds via a "Criegee" adduct, where H_2O_2 adds to the ketone activated by the Sn-Beta, and the formation of dioxiranes or carbonyl oxides as intermediates can be excluded. The complete proposed mechanistic cycle is given in Fig. 2.

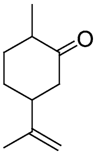
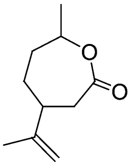
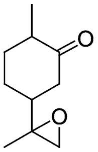
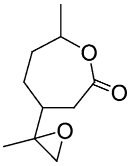
Sn-Beta also carries out successfully the oxidation of aldehydes to esters and the Meerwein–Pondorf–Verley reduction of carbonyl compounds by alcohols [170,171].

10. Transition metal zeolites for selective oxidations using N_2O and oxygen

10.1. N_2O as oxidant

Dehydroxylated and high-silica ZSM-5 zeolites have been used as catalysts for the selective oxidation of aromatic compounds including benzene, chlorobenzene, difluorobenzenes, phenol, styrene, and alkylbenzenes to their corresponding phenol derivatives, using nitrous oxide as oxidant [172,173]. During the steaming of HZSM-5, strong Lewis acid–base pair sites are formed and they were able to hydroxylate benzene with N_2O, producing high yields of phenol (70–80%) with high selectivity and regioselectivity [174]. The catalytic performance of the catalyst can be improved by

Table 4
Baeyer–Villiger oxidation of dihydrocarvone with different catalysts, using H_2O_2 and peracid as oxidant

Oxidant	Reactant conv. (%)	Products selectivity (%)		
				
Sn-Beta/H_2O_2	68	100	0	0
MCPBA[a]	85	11	71	18
Ti-Beta/H_2O_2	46	0	79[b]	0
MTO/H_2O_2[c]	9	30	33	20

[a] Metachloroperbenzoic acid.

[b] The missing 21% comprising products from ring opening of the epoxide.

[c] Methyltrioxorhenium.

incorporating small amounts of iron into the zeolite [175]. Iron ions can be incorporated into the zeolite either during the synthesis or by postsynthesis techniques [176]. An optimal content and distribution of extraframework iron in Fe-silicalites increases phenol selectivity, while high acidity increases benzene conversion, but lowers phenol yield [177].

The industrial application of benzene hydroxylation to give phenol seems close, however before so, the problem of catalyst deactivation with time on stream needs to be solved.

10.2. Oxygen as oxidant

Among the several important unresolved catalytic oxidations using air, the oxyfunctionalization of alkanes and cycloalkanes and the epoxidation of propylene by oxygen are especially relevant.

While the epoxidation of ethene by oxygen is a highly selective industrial process, the epoxidation of propylene is still elusive. The failure to directly epoxidize an allylic olefin such as propylene can be related to the fact that the dissociation energy of the allylic C–H bond in propylene is 77 $\mathrm{kcal\,mol^{-1}}$ while the corresponding dissociation energy of the vinylic C–H bond in ethylene is much larger (112 $\mathrm{kcal\,mol^{-1}}$) [178]. Then, abstraction of the allylic C–H bond by O_2 in propylene is considerably favored compared to ethylene, with the corresponding low epoxide selectivity in the case of propylene. Molecular sieves have been attempted as catalyst for this reaction. Their application is

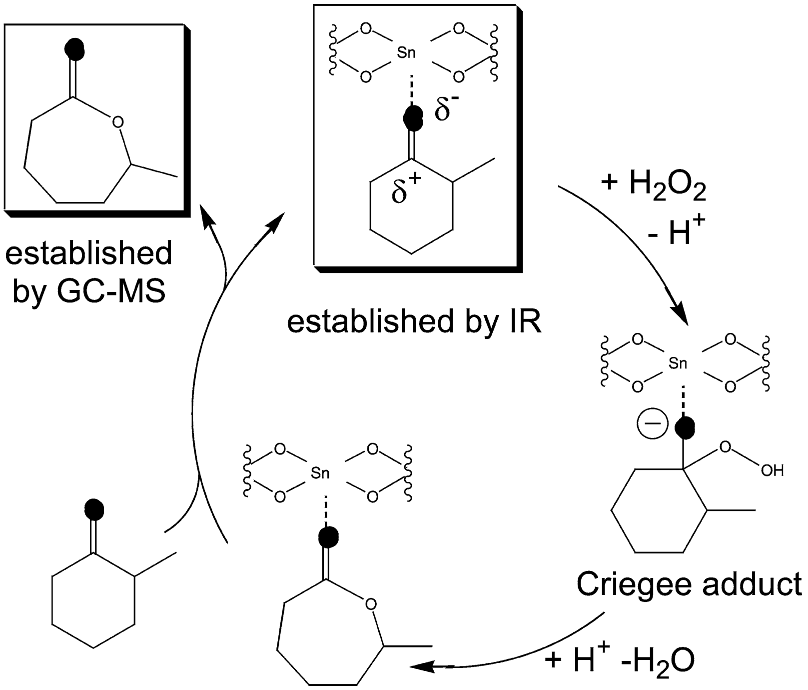
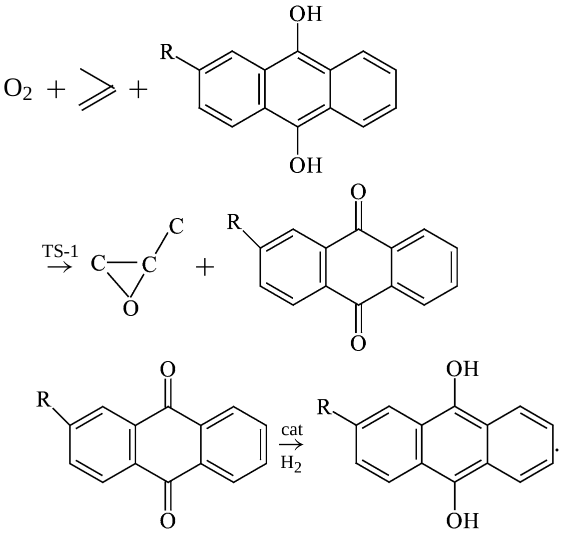


Fig. 2. Mechanism of the Baeyer–Villiger oxidation of 2-methyl-cyclohexanone catalyzed by Sn-Beta.

based on the idea that by means of the adequate active sites, H_2O_2 could be generated in situ from H_2 and O_2, and use this as the oxidant for propylene epoxidation. Thus, Clerici and Ingallina [127,179] were able to epoxidize propylene in the presence of titanium silicalite (TS-1), in one pot, starting with an alkylated anthrahydroquinone with molecular oxygen and propylene:



In this system the organic carrier does not interfere in the catalytic process since it cannot penetrate into the zeolite pores. Yields of propylene oxide, based on starting alkyl anthrahydroquinone, of 78% are claimed. A similar reaction cycle is claimed by ARCO to occur with tetraalkylammonium salts of the anthraquinone-2,6-disulfonic acid in aqueous methanol, giving good yields of propylene oxide.

Propylene epoxidation can be performed using O_2 and H_2 and a bifunctional catalyst formed by Pd and Pt on TS-1. In this system the noble metal catalyzes the formation of H_2O_2 from H_2 and O_2, while the TS-1 zeolite will react the H_2O_2 with propylene to give the epoxide [174]. This process has the handicap of working under conditions close to the explosion limit, and the formation of propane coming from hydrogenation of propylene. On the other hand, when a catalyst formed by gold dispersed on TS-1 is used to epoxidize propylene with H_2O_2 formed in situ by reacting H_2 and O_2 at low temperature, no propane is formed and the selectivity to epoxide is high (99%). Unfortunately, conversion is still too low ($< 2\%$) [180].

With respect to the always interesting oxyfunctionalization of alkanes and cycloalkanes, transition metals such as Cr^{III}, Co^{III}, Mn^{III}, and Fe^{III} substituted into molecular sieve AlPO type structures could, in the presence of O_2 and saturated hydrocarbons, favor the production of the free radicals involved in the oxyfunctionalization process [181]. Care about metal leaching should be taken with these systems [182].

The interest of cyclohexane oxidation for producing cyclohexanone for the production of ε-caprolactam, and adipic acid for producing polyamide fibers and polyurethane resins, has promoted much work on the design of a heterogeneous catalyst for cyclohexane autooxidation. Recently, MnAPO-18 and MnAPO-36 have been reported to be stable catalysts for the autooxidation of cyclohexane when the substrate is used as solvent [183]. Possibilities of leaching, especially at higher levels of conversion, have to be further studied.

Finally, the strong electric fields present inside the supercages of Y zeolite, particularly those ion-exchanged with alkaline earth cations, can stabilize the collisional charge-transfer complexes between molecular oxygen and alkanes, alkenes, and aromatic hydrocarbons, formed by irradiation [184–186], or by thermal activation [187]. This is an interesting concept that should be further investigated. So far, the process becomes limited by the desorption of the product from the catalyst.

11. Conclusions and perspectives in catalysis

Zeolites have been shown to be useful catalysts in a large variety of reactions, from acid to base and redox catalysis. We have seen that they will offer new opportunities for reactions in the field of chemical and fine chemicals if, besides the nature of active sites and dimensions and shape of the pores, one is able to tune the adsorption properties and local geometry of the active sites. However, for many important applications, the size of the zeolitic pores are too small to react the bulky desired molecules. Thus, new zeolites with larger pores have to be synthesized. If we refer exclusively to zeolites, the maximum pore diameter corresponds to UTD-1 with 1.0×0.75 nm [188,189]. This is a unidimensional pore zeolite that, while interesting for some particular applications, can present limitations due to pore blocking. For improving the catalytic properties of zeolites when dealing with bulky molecules, the following possibilities can be seen:

- Synthesize zeolites with nanocrystals.
- Synthesize delaminated zeolites.
- Synthesize ultra-large-pore zeolites.

Nanocrystalline zeolites allow large ratios of external to internal surfaces to be achieved. Then the reactions will occur at the external surface-pore mouth of the zeolite. In this case, however, stability of the zeolite upon catalyst regeneration can be an issue. Furthermore, for many bulky reactants it will still be difficult to reach active sites located at the pore mouth. Preparation of mesoporous–microporous hybrid structures can be a good complement to the use of nanocrystalline zeolites [190].

Delaminated zeolites [191] present a very large external surface ($> 600\ m^2\ g^{-1}$) with good accessibility to active sites for bulky molecules of interest in oil refining, chemicals, and fine chemicals. Delaminated zeolites are stable toward high-temperature calcination. For more demanding regeneration conditions, the level of delamination, i.e., the size of the layers, could be controlled and in this way the hydrothermal stability of the delaminated zeolite could be improved. Further work in this area is needed.

Finally, the most direct way to expand the possibilities of zeolites in catalysis will be to synthesize new structures (if possible with a tridimensional arrange of connected pores) with ultralarge pores ($\geqslant 1.0$ nm). Some leads toward this can be found in [192,193]. Recently, a new large-pore zeolite with a tridimensional system of interconnected pores with pore diameter 0.74 nm has been synthesized by combining a large rigid organic structure directing agent that can make clusters of various molecules and the directing property of Ge toward the formation of double four-member rings [194]. It appears to us that by aiming toward the formation of three- and four-member ring secondary building units by means of specific cations–anions, and the use of large and rigid organic-structure-directing agents it may be possible to synthesize zeolites with larger pores. Another possibility is to combine framework cations that may coordinate tetrahedrally and pentahedrally, leading to new structures with very large pores [195].

New shape selectivity effects should be possible by synthesizing tridimensional medium-pore-size zeolites with pores formed by 9- or 9- and 10-member rings. The deliberated epitaxial isotactic overgrowth of two zeolite phases at the micrometer scale has been demonstrated [196] and this can also offer new reaction selectivity features [197].

The synthesis of a pure enantiomer of a chiral zeolite structure will be a major breakthrough in the field that can lead into new separation and catalytic applications. However, one should take into account that the size of the chiral fragment of the zeolite can be too large for the prochiral molecules that can fit into the channels.

Finally, Lewis-acid-catalyzed reactions (also including oxidations) using zeolites still offer an open field. This will be more so if chiral organic molecules can be coordinated with the Lewis acid sites within the zeolites.

Acknowledgment

Financial support by the Spanish CICYT (MAT2000-1392) is gratefully acknowledged.

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