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ZEOLITE CATALYSTS FOR CLEANER TECHNOLOGIES

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INTRODUCTION

The name of zeolites, which originates from the Greek words *zeo* (to boil) and *lithos* (stone), was given some 250 years ago to a family of minerals (hydrated aluminosilicates) that exhibited intumescence when heated in a flame.¹ However, the history of zeolites really began 60 years ago with the development of synthesis methods. Commercial applications in three main fields—ion exchange, adsorption, and catalysis—were rapidly developed, the corresponding processes being more environmentally friendly than their predecessors.

Thus, the largest use of zeolites (~70%) is as a water-softener substitute for sodium tripolyphosphate (STPP) in laundry detergents.² Contrary to STPP, which disrupts the biological equilibrium of rivers and lakes by eutrophication, the NaA zeolite, which is now generally employed, has no negative effect on the environment. Furthermore, the high efficiency of zeolites for the ultimate drying of gases and liquids led to a large variety of applications; separation of isomers (e.g., *n*-butane/isobutane) through adsorption over zeolites was substituted for the classic methods of distillation and crystallization, which consume energy.

The highest market value for zeolites, however, is in the field of catalysis: zeolites are now involved as basis components of most of the catalysts used in the production of fuels and petrochemicals; moreover they are playing an increasing

role in the synthesis of intermediate and fine chemicals, as well as in pollution abatement.³ This is due to three main factors:

1. The molecular-size pore system of zeolites, in which the catalytic reactions occur: zeolite catalysts can be considered as a succession of *nano or molecular reactors* (their channels, cages, or channel intersections). The result is that the rate, selectivity, and stability of all the zeolite catalyzed reactions are affected by the shape and size of the nano reactors and of their apertures. This effect has two main origins: (i) *spatial constraints* on the diffusion of reactant or product molecules or on the formation of intermediates or transition states that limit the formation of undesired products; (ii) *confinement* within the micropores of reactant molecules, with a positive effect on the rates of the reaction, especially the bimolecular ones, but also of product molecules with sometimes autoinhibition of the desired reaction. These characteristics of zeolite catalyzed reactions are generally grouped under the label *shape selectivity*, which was proposed 45 years ago by Weisz and Frillette.⁴ This name, which considers only the shape of the micropores, but not their size and that of their apertures, as well as only the selectivity, although both reaction rate and stability are also significantly affected, could seem too restrictive. However, it has the great advantage of being simple and striking. The concept of shape selectivity, which was at the origin of the design and development of many processes, remains an important source for conceiving new processes and improving existing ones. This is clearly demonstrated by the major breakthrough in the field established by the discovery that the shape selective properties of zeolites were not limited to their inner micropores, but could also originate from the external surface of their crystallites. This discovery that was made possible by the development of methods for the synthesis of very small crystallites ($\sim 20\text{--}50\text{ nm}$ instead of $0.3\text{--}1\text{ }\mu\text{m}$ for conventional zeolites), hence with a large external surface, has already led to commercial applications.

2. *The rich variety of active sites* that can be present in zeolites: (i) protonic acidic sites, which catalyze acid reactions; (ii) Lewis-acid sites, which often act in association with basic sites (acid–base catalysis); (iii) basic sites; (iv) redox sites, incorporated either in the zeolite framework (e.g., Ti of titanosilicates) or in the channels or cages (e.g., Pt clusters, metal complexes). Moreover, redox and acidic or basic sites can act in a concerted way for catalyzing bifunctional processes.

3. *The large number of different zeolites* that have been synthesized (more than 130), as well as *the variety of well-mastered postsynthesis treatments* that have been developed for tailoring their composition, porosity and acidity. Other characteristics of zeolites—their easy handling (no corrosivity even for the most acidic ones, etc.) and setup in continuous processes, their high thermal stability, which allows their use under a wide range of operating conditions, as well as their regeneration by coke oxidation, etc., have also played a significant role in the development of zeolite-catalyzed processes.

After a short description of the main features of zeolites, the significant contribution of zeolite catalysts in green chemistry will be shown in examples of commercial or the potential processes of refining, petrochemicals, and fine chemicals involving acid or metal acid bifunctional catalysts.

12.1 MAIN ZEOLITES FEATURES

12.1.1 Description and Denomination of Zeolites

Zeolites are crystalline aluminosilicates based on a three-dimensional arrangement of TO_4 tetrahedra (SiO_4 or AlO_4^-) connected through their O atoms to form sub-units and then large lattices by repeating identical building blocks (unit cells, u.c.). The structure formula of zeolites (i.e., the u.c. composition) is the following: $\text{M}_{x/n} (\text{AlO}_2)_x (\text{SiO}_2)_y$, where n is the valence of M (cation or proton), $x + y$ the number of tetrahedra per u.c., and y/x the atomic Si/Al ratio, which may vary from a minimal value of 1 (Lowenstein rule) to infinite.

Most of the zeolites can be classified into three categories according to the number of O (or T) atoms in the largest micropore apertures: 8-member-ring (8-MR) or small-pore zeolites with 8 O atoms apertures with free diameters of 0.3–0.45 nm; -10-MR or medium-pore zeolites, with free diameters 0.45–0.60 nm; -12-MR or large-pore zeolites, with free diameters of 0.6–0.8 nm. A comparison between these pore openings and the kinetic diameter of organic molecules clearly shows that zeolites can be used for *molecular sieving*.

Zeolite structures are designated by a three capital-letter code,⁵ for example, FAU stands for the faujasite structure, to which the well-known X and Y zeolites belong. A very useful short notation is used for the description of the pore system(s): each pore network is characterized by the channel directions, the number of atoms (in bold type) in the apertures, the crystallographic free diameter of the aperture (in Å), asterisks (1, 2, or 3) indicating whether the systems is one-, two-, or three-dimensional. To completely specify the pore system, the eventual presence of cages (or channel intersections) should be indicated, along with their

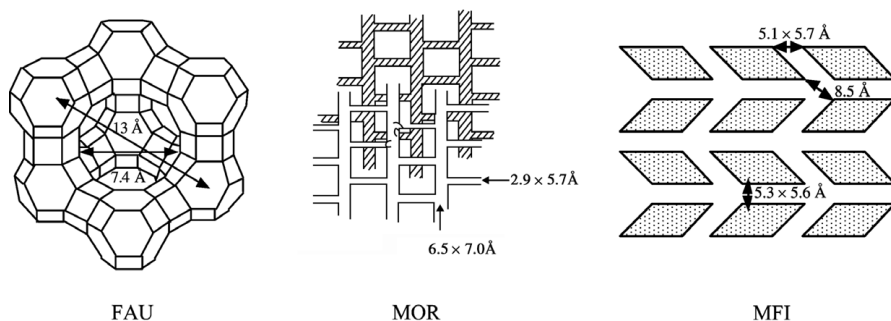


Figure 12.1 Pore structure of three zeolites largely used in catalytic processes.

TABLE 12.1 Commercially Used Zeolites

Structure Code (other names)	N _T /u.c.	Channels	Applications
(a) <i>Large Pore Zeolites</i>			
BEA	64	<100> 12 6, 6 × 6,7** ↔[001] 12 5,6 × 5,6*	Catal: cumene synthesis, anisole acetylation
FAU (X,Y)	192	<111> 12 7,4 × 7,4***	X-Drying, separation (<i>p</i> -xylene) Y-Separation, catalysis (FCC, Hydrocracking, etc.)
LTL	36	[001] 12 7,1 × 7,1*	Catal: aromatization
MOR	48	[001] 12 6,5 × 7,0* ↔ {[010] 8 3,4 × 4,8 ↔ [001] 8 2,6 × 5,7}*	Catal: isomerization of C ₅ –C ₆ alkanes, of C ₈ aromatics
(b) <i>Medium Pore Zeolites</i>			
AEL (SAPO-11)	—	[001] 10 4,0 × 6,5*	Catal: isodewaxing
FER	36	[001] 10 4,2 × 5,4* ↔[010] 8 3,5 × 4,8*	Catal: isomerization of <i>n</i> -butenes
MFI (ZSM-5)	96	{[100] 10 5,1 × 5,5 ↔ [010] 10 5,3 × 5,6}***	Catal: MTO, FCC, selective synthesis of alkylbenzene, (ethylbenzene, paraxylene, etc.)
MWW (MCM-22)	72	⊥ [001] 10 4,0 × 5,5** ⊥ [001] 10 4,1 × 5,1**	Catal: synthesis of ethylbenzene, of cumene
TON (ZSM-22)	24	[001] 10 4,6 × 5,7	Catal: isodewaxing
(c) <i>Small Pore Zeolites</i>			
CHA (SAPO-34)	—	⊥ [001] 8 3,8 × 3,8***	Catal: MTO
LTA (3A, 4A, 5A)	24	<100> 8 4,1 × 4,1***	Ion exchange: detergents separation (<i>n</i> , isoalkanes) Drying

Note: N_T/u.c.: number of T(Si + Al) atoms per unit cell.

dimensions. The International Zeolite Association (IZA) coding of the main commercially used zeolites is given in Table 12.1. Figure 12.1 shows as an example the pore structure of the three zeolites that are the most used in catalysis.

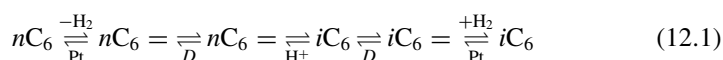
12.1.2 Acid and Bifunctional Metal/Acid Catalysis: Active Sites

Most of the commercial zeolite catalyzed processes occur either through acid catalysis: fluid catalytic cracking (FCC), aromatic alkylation, methanol to olefins (MTO),

acetylation, and so on; or through hydrogenating/acid bifunctional catalysis: hydroisomerization of alkanes, hydrocracking, dewaxing, hydroisomerization of the C₈ aromatic cut, and so on. Protonic zeolites are generally used, the active sites being the protons that are associated with the bridging hydroxyl groups Al (OH) Si. Therefore, their maximum concentration is equal to that of the framework Al atoms; however, the actual concentration is always smaller due to the remaining cations or to dehydroxylation and dealumination during the catalyst activation.

The rate of acidic reactions depends on the concentration of accessible protonic acid sites, on their strength, and for certain bimolecular reactions, such as hydrogen transfer, on their proximity. The concentration (and inversely the proximity) of protonic sites can be adjusted either during the synthesis (choice of the Si/Al ratio) or through postsynthesis treatment of the zeolite: ion exchange, dealumination by various methods, that is, by steaming, acid leaching, or isomorphic substitution by silicon compounds. These postsynthesis treatments may also modify the acid strength of the zeolites, thus dealumination can have a positive effect on the acid strength, the "isolated" protonic sites (no next nearest neighbours) having the maximum acid strength,⁶ and extraframework Al species created by steaming (which are Lewis-acid sites) increasing the acid strength of neighboring protonic sites.⁷ These post-synthesis treatments which are well-mastered allowed the adequate adjustment of the zeolite acidity to the catalysis of the desired reactions.

Noble metals (e.g., Pt) can be introduced within the micropores of zeolites by exchange with a complex cation (e.g., Pt(NH₃)₄²⁺) followed by calcination and reduction. This mode of introduction generally leads to very small clusters of Pt (high Pt dispersion) located within the micropores. Pt supported on acid zeolites are used as bifunctional catalysts in many commercial processes. The desired transformations involve a series of catalytic and diffusion (*D*) steps,⁸ as shown in *n*-hexane isomerization over Pt acidic zeolite (Equation 12.1).



Under the operating conditions, the reaction intermediates (*n*-hexenes and *i*-hexenes in *n*-hexane isomerization) are thermodynamically very adverse, hence appear only as traces in the products. These intermediates (which are generally olefinic) are highly reactive in acid catalysis, which explains that the rates of bifunctional catalysis transformations are relatively high. The activity, stability, and selectivity of bifunctional zeolite catalysts depend mainly on three parameters: the zeolite pore structure, the balance between hydrogenating and acid functions, and their intimacy.⁹ In most of the commercial processes, the balance is in favor of the hydrogenation function, that is, the transformations are limited by the acid function.

Bifunctional catalysis is one of the most important routes to green (more economical and more environmentally friendly) processes.¹⁰ Indeed, the deactivation of bifunctional catalysts by coking is much slower than that of monofunctional catalysts and their selectivity generally higher (e.g., hydrocracking compared to

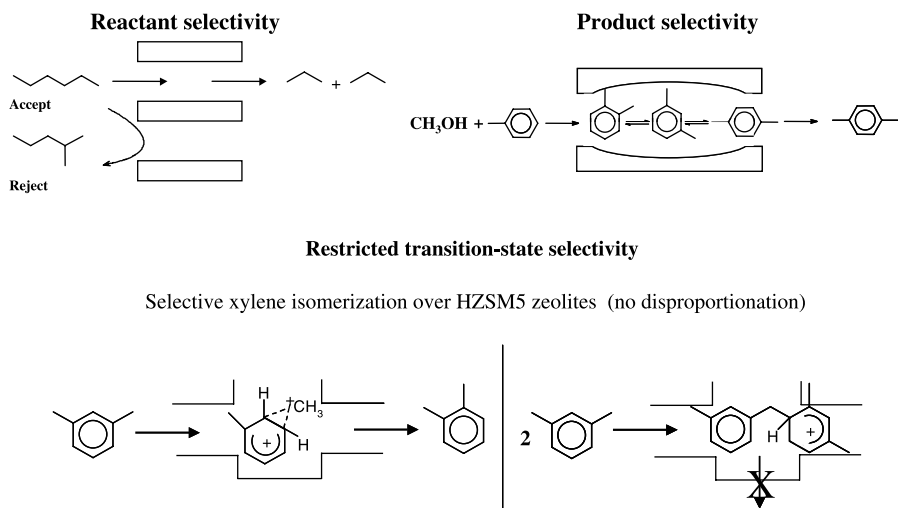


Figure 12.2 Shape selectivity of zeolites.

cracking). Moreover, bifunctional catalysts can be used in one-pot multistep synthesis with therefore a reduction in the number of chemical and separation steps, hence, of waste production.

12.1.3 Shape Selectivity

There are four widely accepted theories of shape selectivity:^{11–13} reactant shape selectivity (RSS), product shape selectivity (PSS), transition state selectivity (TSS) (Figure 12.2), and concentration effect; all of them are based on the hypothesis that the reactions occur within the zeolite micropores only. As indicated earlier, this hypothesis is often verified, the external surface area of the commonly used zeolites being much lower (one to two orders of magnitude) than their internal “surface area.”

12.1.3.1 Shape Selectivity Due to Molecular Sieving. The simplest types of shape selectivity are related to the impossibility for certain molecules of a reactant mixture to enter the micropores (RSS) or for certain product molecules to exit from these pores (PSS). In practice, RSS and PSS are observed not only when the molecule size is larger than the pore openings (size exclusion) but also when their diffusion rate is significantly lower (by two orders of magnitude) than that of the other molecules.

12.1.3.2 Spatioselectivity or Transition State Selectivity. TSS occurs when the formation of reaction intermediates (and/or transition states) is sterically limited by the space available near the active sites. Contrary to molecular sieving, TSS does not depend on the size of pore openings, but depends on the size and shape

of cages, channels, and channel intersections. TSS often plays a significant role when the reactant(s) may undergo both monomolecular and bimolecular reactions, the latter involving much bulkier intermediates and/or transition states than the former.

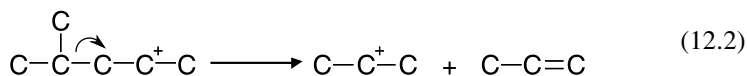
12.1.3.3 Shape Selectivity Related to Molecular Concentration in Zeolite Micropores. The interaction between organic molecules and the walls of molecular-size micropores is very strong and zeolites may be considered as *solid solvents*.¹⁴ Therefore, the concentration of reactants in the zeolite micropores is considerably higher than in the gas phase with a significant positive effect on the reaction rates, this effect being more pronounced on bimolecular than on monomolecular reactions. This concentration of molecules in zeolite micropores is largely responsible for the observation that zeolite catalysts are much more active (10 to 10,000 times) than conventional catalysts. It is also responsible for the completely different distribution of hydrocarbons in the gasoline FCC over zeolites and amorphous silica alumina catalysts: more aromatics and alkanes with zeolites at the expense of naphthenes and alkenes owing to a higher ratio between the two major reactions in FCC, that is, hydrogen transfer (bimolecular) and cracking (monomolecular).

12.1.3.4 Other Types of Shape Selectivity. Various other types of shape selectivity have been proposed, some of them requiring additional demonstration. This is not the case for the shape selectivity of the external surface of zeolite crystallites: nest effect, pore mouth, and key lock catalysis, which is discussed in the examples in the next section.

12.2 RECENT DEVELOPMENTS

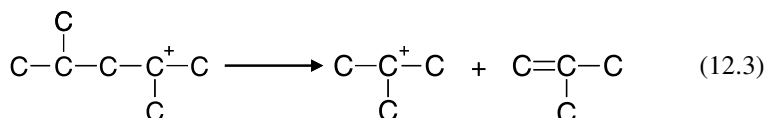
12.2.1 Isodewaxing

To meet the cold flow requirements, the high molecular-weight linear paraffins (waxes) have to be removed from distillates and base oils. This removal, called *dewaxing*, might be achieved either by solvent extraction or by selective catalytic conversion: hydrocracking or hydroisomerization over zeolite catalysts.¹⁵ Hydroisomerization, which decreases the pour point without decreasing the product yield, is the most advantageous. However, whereas it is very easy to selectively isomerize C₅–C₆ *n*-alkanes over bifunctional zeolite catalysts (such as Pt HMOR), this is not generally the case for heavier hydrocarbons, because of a fast secondary cracking of branched alkanes. Indeed, with C₆ alkanes, only the very slow C- type acid cracking (Equation 12.2) can occur



whereas with C₈⁺ alkanes, the very fast A cracking, which involves two tertiary

carbenium ions intermediates, appears:



This A cracking was shown to be 20 times faster than the rearrangement of type B involved in *n*-alkane hydroisomerization.

As a consequence, over ideal bifunctional Pt HFAU catalysts, that is, over catalysts on which acid isomerization and cracking of alkene intermediates are the limiting steps, the maximum yield of isodecanes that could be obtained is not very high ($\sim 50\%$).¹⁶ The maximum yield is even lower ($\sim 20\%$) with HMFI as the acidic component of the bifunctional catalyst; this can be ascribed to limitations in the diffusion of isodecene intermediates, which undergo secondary cracking during their long residence time in the narrow pores of HMFI. However, with another medium-pore zeolite (TON) as acid component of the bifunctional catalyst, an exceptionally high yield in isodecane can be obtained,¹⁷ and this practically without deactivation. This seems all the more surprising as (1) TON is a monodimensional zeolite and the pore blockage by carbonaceous deposits of these type of zeolites is known to be very fast, and (2) TON has pore openings smaller than the three-dimensional MFI zeolites (Table 12.1), which should be even more favorable for secondary cracking. Whereas the classic reaction scheme



found with bifunctional catalysts, can also be observed with Pt TON, the maximum in monobranched (*n*-C₉), bibranched (*dm*-C₈) are higher and much better separated. Therefore, long-chain *n* alkanes can be very selectively transformed into isomers, but also to monobranched or to multibranched isomers. Since it is only the first methyl group that causes a significant decrease in the pour point of alkanes (from 30°C to 60°C), this possibility to selectively form monobranched isomers seems in favor to the use of Pt TON as isodewaxing catalyst. However to minimize the pour point, the methyl branch has to be preferentially located toward the center of the chain,¹⁵ although isomerization of *n*-alkanes was found to result in selective 2-methylbranching up to high conversion levels.¹⁷ Subsequent isomerization of 2-methylalkanes by alkyl shift (which occurs very fast over bifunctional large-pore-based catalyst) seems desirable.

Because molecular graphics suggested that isomerization of decene intermediates could not occur entirely inside the TON channels,¹⁸ it was theorized that this reaction occurred at the mouth of the micropores. This pore-mouth catalysis was confirmed¹⁹ by characterization of Pt TON samples recovered after various time-on-stream (TOS). The quasi-immediate retention of 1.5–2.0 wt % of carbonaceous compounds on the catalysts could be observed, these compounds causing a quasi-total blockage of the access of nitrogen (hence, of reactants) to the TON

channels. These carbonaceous compounds were demonstrated to be essentially constituted by C_{12} – C_{20} linear and monobranched alkanes trapped within the zeolite channels.

In agreement with this pore blockage, it was suggested that isomerization would be catalyzed by protonic sites at the mouth of the channels; however, another possibility might be that the molecules of products trapped within the micropores near the external surface were the active species. Indeed, a simple mechanism, in which active sites are tertiary carbenium ions formed at the pore mouth by adsorption of methylalkenes trapped in the zeolite pores during the first minutes of reaction, can be theorized.¹⁹ This mechanism involves only very simple steps: A isomerization (through alkyl shift), hydride transfer, A cracking, which is simple than the limiting step of isomerization (B-type) catalyzed by the protonic-acid sites located at the pore mouth. Moreover, contrary to this latter mechanism, it requires no diffusion of alkene intermediate molecules in the narrow zeolite channels (Figure 12.3).

High selectivity in hydroisomerization of long-chain alkanes can also be obtained with the other medium-pore zeolites or silicoaluminophosphates similar to TON, that is, having a monodimensional pore system with small apertures: MTT, FER, SAPO 11. Commercial processes were developed using these molecular sieves as catalysts, in particular Isodewaxing by Chevron, Mobil's Selective Dewaxing (MSDW), and Wax Isomerization (MWI) by Exxon Mobil. These

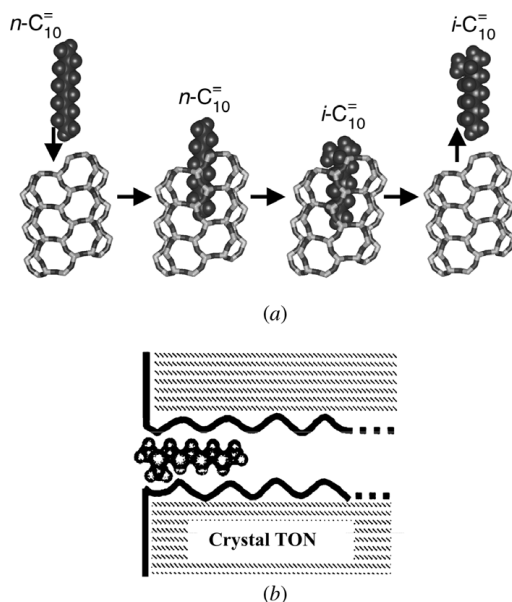


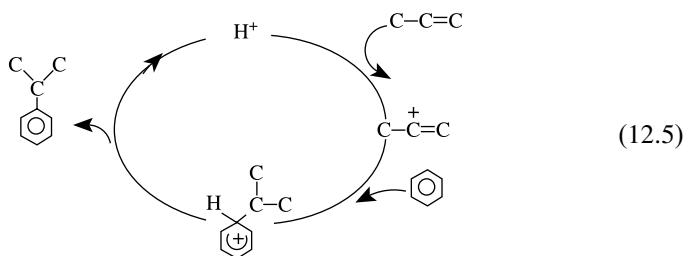
Figure 12.3 Mechanisms of n -decane isomerization over Pt HTON. (a) Protonic sites at the pore mouth. (b) Monobranched alkenes (formed from “coke” molecules) adsorbed on protonic sites at the pore mouth.

processes are more efficient than those based on solvent extraction or on selective hydrocracking. Thus, results obtained on pilot plants showed that for similar values of the pour point of the product (-12°C), the yield was much higher (90.5 wt %) with isodewaxing than with dewaxing by hydrocracking; moreover, the viscosity index VI (the temperature dependence of the viscosity, a high VI indicating a low dependence) was of 105 instead of 92.¹⁵

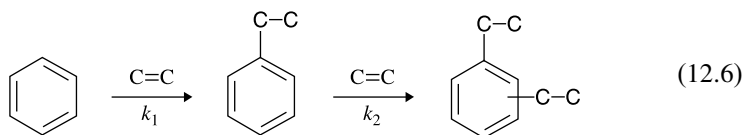
12.2.2 Ethylbenzene and Cumene Production

12.2.2.1 Generalities. Alkylation of aromatic compounds is practiced commercially on a large scale. The major products are ethylbenzene converted into styrene for polymer use and cumene (isopropylbenzene), a precursor to acetone and phenol.^{20, 21} Alkylation of benzene by ethylene or propylene is an electrophilic substitution catalyzed by protonic acid sites. Acidic halides such as AlCl_3 , which are typically Lewis acids, have little or no activity when used in a pure state; they become active by addition of co-catalysts such as hydrochloric acid, which interact with AlCl_3 to generate a strong protonic acidity ($\text{AlCl}_4^- \text{H}^+$).

The mechanism of catalytic alkylation is later in the example of benzene isopropylation:



Ethylation, which involves an unstable ethylcarbenium ion as intermediate, is much slower (1500 times over AlCl_3) than isopropylation. It is also the case in benzene alkylation with propene for the undesired formation of *n*-propylbenzene, which involves a primary *n*-propyl carbocation. Furthermore, as alkyl substituents activate the aromatic ring, consecutive alkylation of the primary product occurs with a greater rate than the first alkylation step ($k_2 > k_1$).



There are several means to maximize the yield in the desired monoalkylation product: high aromatic/alkylation agent ratio, association of a transalkylation unit to the alkylation unit, and use of a shape selective zeolite as catalyst.

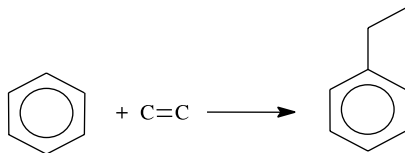


Figure 12.4 Ethylbenzene synthesis. Commercial processes. **$\text{AlCl}_3 + \text{HCl}$ catalyst (1950):** AlCl_3 corrosivity and problems associated with safe handling and disposal. For one tonne of EB, consumption of 2–4 kg catalyst, 1 kg of HCl, and 5 kg of caustic solution with production of salts. **Zeolite catalysts:** (1) 1980 Mobil Badger vapor-phase process MFI (ZSM5) 370–420°C, 7–27 bar, $\text{B/C}_2 = 5\text{--}20$, WHSV 300–400 h^{-1} , recycling of DEB, yield > 99.5%, cycle length: 1 year; high-energy efficiency. (2) 1995 EB Max liquid-phase process MWW (MCM22) 200°C, $\text{B/C}_2 = 3.5$, Yield > 99.9%, cycle length > 3 years.

12.2.2.2 Toward Cleaner Processes. AlCl_3 was the first catalyst used for ethylbenzene production, and nearly 40% of the ethylbenzene capacity still utilizes the AlCl_3 process. There are serious problems due to the corrosivity of AlCl_3 and to waste production (Figure.12.4). This has led most manufacturers to move toward zeolite catalyzed processes that do not present these inconveniencies. Figure 12.4 shows the significant improvements caused by the substitution of AlCl_3 by the MFI zeolite (Mobil Badger process, 1980), and then by the MWW (MCM-22) zeolite (EB Max process, 1995). The Mobil Badger process operates in the vapor phase at a high temperature. One of the initial problems was the relatively fast deactivation of the MFI zeolite by coking with the need for frequent regenerations. This problem was solved in the second and third (1986, 1991) generations of processes, the cycle lengths passing from 60 days to more than one year. A very high ethylbenzene yield (>99.5%) can be obtained. Other advantages over the AlCl_3 process were the recovery of practically all the heat of reaction ($\Delta H = -114 \text{ kJ}\cdot\text{mol}^{-1}$) as medium or low-pressure vapor, and the possibility to use dilute ethylene as feed. EB Max is a liquid-phase process. The MWW zeolite is very stable (cycle lengths > 3 years) and very selective to monoalkylate, which allows the process to use low feed ratios of benzene to ethylene. The undesired diethylbenzene products undergo transalkylation with benzene in an additional reactor operating either in liquid or in gas phase.²¹

Up to 10 years ago, cumene was essentially produced by isopropylation of benzene using solid phosphoric acid (SPA), actually phosphoric acid supported on kieselgur, or AlCl_3 (for only a small number of plants). Small amounts of water have to be continuously fed to the reactor in order to maintain the desired level of activity; consequently, there is a continuous release of corrosive phosphoric acid. The other drawbacks of the SPA process deal with the disposal of the used catalyst as well as with the production of undesired bi- and triisopropyl benzenes (4–5 wt. %). Greener processes based on zeolite catalysts have been recently licensed by DOW (dealuminated mordenite), Enichem (BEA), and Mobil Badger (MWW). Higher cumene yields can be obtained owing to the attachment to the alkylation process of a transalkylation unit for converting the diisopropylbenzene by-product to cumene.

12.2.2.3 Alkylation over the MWW Zeolite. The MWW (or MCM-22) zeolite developed by Mobil as catalyst for ethylbenzene and cumene production deserves particular attention. Indeed, this zeolite presents unique structural features (Figure 12.5). Its structure is constituted of *three independent pore systems*:²¹ large supercages (inner diameter of 7.1 Å defined by a 12-member-ring [12-MR], height 18.2 Å) each connected to six others through 10-MR apertures (4.0 Å × 5.5 Å), bidimensional sinusoidal channels (10-MR, 4.1 × 5.1 Å),²² and large hemisupercages (7.1 Å Ø, 7.0 Å) on the external surface.²³

Acid sites were shown to be located in the three-pore system of protonated samples (HMWW), and methods were recently proposed for determining the distribution of these sites as well as their respective role in *o*-, *m*-, and *p*-xylene transformations.²⁴ While xylene transformation was shown to occur in the three locations, benzene alkylation with ethylene was catalyzed by the acidic sites of the external hemicups only.²⁵ Indeed, the activity for this reaction is completely suppressed by adding a base molecule (collidine) to the feed that is too bulky to enter the inner micropores. Moreover, adsorption experiments show that collidine does not influence the rate of ethylbenzene adsorption, so that the suppression of alkylation activity was not caused by pore mouth blocking.²⁵

However, by using a model reaction (gas-phase toluene alkylation with propene) we have recently demonstrated²⁶ that initially the protonic sites of the supercages catalyze the formation of heavy alkylaromatics, those of the sinusoidal channels, the transformation of the olefin through an oligomerization–cracking process, and the formation of a small amount of alkylaromatics. A large part of these alkylaromatics remain trapped within the inner micropores, causing a quasi-immediate blockage of their access by reactant molecules; this shows that only the protonic sites of the external hemicages seem to be active in ethylbenzene formation. The high selectivity of these sites to monoalkylates and their high

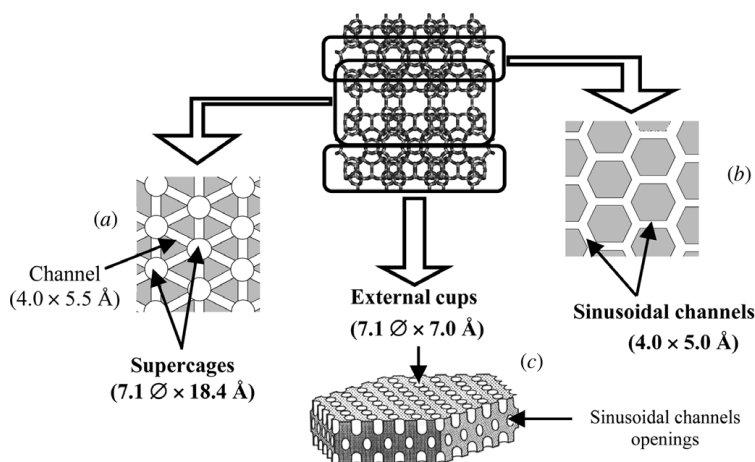


Figure 12.5 Pore structure of MCM22 (MWW).

stability are most likely due to the ease of desorption of product molecules from the large external hemicages.

12.2.3 Fine Chemicals Synthesis

Significant advances remain to be accomplished to make the fine chemical processes environmentally friendly: indeed, the so-called environmental factor²⁷ that is, the ratio between the amounts of waste and product, is still between 5 and 50, that is, 50 to 500 times greater than in refining and petrochemicals. Of course, this is because the fine chemicals synthesis requires a significant number of chemical and separation steps, but also because most of the chemical steps are carried out in batch reactors in homogeneous phase, either stoichiometrically or by using acid catalysts such as H_2SO_4 or AlCl_3 . These acids, which are not reusable, have to be neutralized, which generates a large amount of valueless salts.

There is an urgent need to substitute cleaner technologies, such as those based on heterogeneous catalysis, for these polluting technologies. Indeed, solid catalysts such as zeolites offer many advantages, in particular, easy recovery of reaction products, safe handling, easy setup of continuous processes, and regenerability. Here we show that acid zeolites that, due to their shape-selective properties and the easy tailoring of their active sites and porosity, are the major catalysts in refining and petrochemicals should play a significant role in fine chemical synthesis in the near future.

However, some characteristics of the reactant and product (and solvent) molecules used in the reactions of fine chemical synthesis have to be considered: their large size, their low thermal stability, and their polarity. The small size of the micropores limits the use of zeolites to the synthesis of relatively small molecules; solutions to overstep this limitation have been found with the development of larger (mesoporous) molecular sieves and of nanocrystallite zeolites, the reaction then occurring on the large external surface. The low thermal stability of the molecules leads to operation at a low temperature, often in the liquid phase. Last, as will be shown in the first example (Section 12.2.3.1), the differences in polarity between reactant(s), product(s), and solvent molecules have to be considered for optimizing both the zeolite catalyst and the operating conditions.

12.2.3.1 Acetylation of Arenes with Acetic Anhydride. Arylketones are generally prepared by acylation of aromatics or by the related Fries rearrangement. These ketones are important intermediates in the synthesis of fragrances of the musk type and of pharmaceuticals such as paracetamol, ibuprofen, and S-naproxen.²⁸ Acylation processes are often carried out in the liquid phase by using batch reactors with corrosive metal chlorides, such as AlCl_3 as catalysts and acid chlorides as acylating agents. A characteristic of this reaction is the formation of a stable 1:1 molar adduct with the catalyst, which generates serious environmental problems: use of more than a stoichiometric amount of the “catalyst,” necessary hydrolysis of the adduct for recovering the desired ketone with

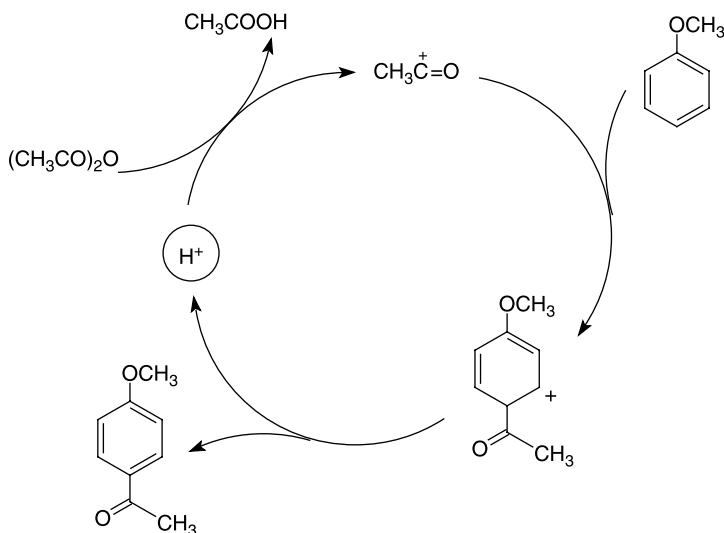


Figure 12.6 Mechanism of anisole acetylation over protonic zeolites.

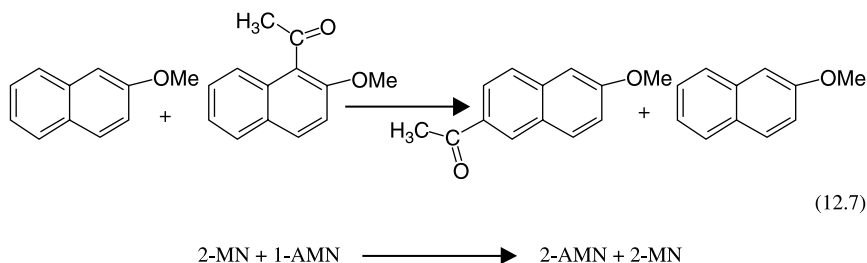
destruction of the catalyst, and production of a large amount of HCl (more than 4 mol per mol of ketone produced) with corrosion problems and final production of valueless salts. All that makes the substitution of AlCl_3 by acid zeolites highly desirable, and also that of acetyl chloride by acetic anhydride or acetic acid.

The acetylation over protonic zeolites of aromatic substrates with acetic anhydride was widely investigated. Essentially HFAU, HBEA, and HMFI were used as catalysts, most of the reactions being carried out in batch reactors, often in the presence of solvent. Owing to the deactivation effect of the acetyl group, acetylation is limited to monoacetylated products. As could be expected in electrophilic substitution, the reactivity of the aromatic substrates is strongly influenced by the substituents, for example, anisole > *m*-xylene > toluene > fluorobenzene.²⁹ Moreover, with the poorly activated substrates (*m*-xylene, toluene, and fluorobenzene) there is a quasi-immediate inhibition of the reaction. It is not the case with activated substrates such as anisole and more generally aromatic ethers. It is why we have chosen the acetylation of anisole and 2-methoxynaphtalene as an example.

It is generally admitted that over zeolites, acetylation of aromatic substrates with acetic anhydride (AA) is catalyzed by protonic acid sites. The direct participation of Lewis sites was excluded by using two BEA samples with similar protonic acidities, but with very different Lewis acidities: indeed, these samples were shown to have quasi-similar activities.³⁰ The currently accepted mechanism is shown in Figure 12.6 for the anisole acetylation example. The limiting step of the process is the attack of anisole molecules by acylium ions.

Whatever the zeolite, 4-methoxyacetophenone is largely predominant (>98%), which indicates that this selective formation is not due to shape-selectivity effects, but is a characteristic of the reaction. In contrast, the selectivity of

2-methylnaphtalene (2-MN) acetylation depends very much on the zeolite employed: over FAU zeolites, acetylation of 2-MN occurs very selectively at the very active C1 position with formation of 1-acetyl-2-methoxynaphtalene (1-AMN), whereas with other large-pore zeolites with smaller-pore apertures (BEA, MTW, ITQ7), the desired 2-acetyl-6-methoxynaphtalene product, 2-AMN (precursor of the anti-inflammatory *S*-naproxen), also appears as a primary product. Moreover, at long reaction times, 1-AMN isomerizes into 2-AMN. This isomerization is much faster in the presence of 2-MN than in its absence, causing the following intermolecular (transacetylation) mechanism to be proposed:³¹

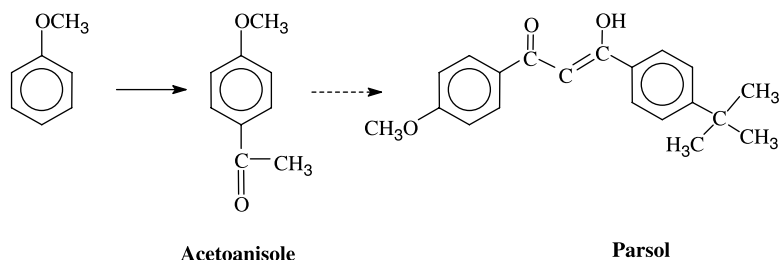


The location of 2-MN acetylation over HBEA zeolites was largely debated. Some authors claimed that the bulkier isomer (1-AMN) could be formed only on the external surface, and the linear one (2-AMN) both within the micropores and on the external surface, while other than that both isomers were essentially formed within the micropores. The second proposal seems to be more likely; indeed, adsorption experiments showed that 1-AMN could enter the micropores of HBEA and even those of MFI, a medium-pore zeolite.³²

Kinetic studies of the acetylation of several ary ethers were carried out over HBEA zeolites. The main conclusion is that the rate and stability of the reactions are determined by the competition between reactant(s) and product(s) molecules for adsorption within the zeolite micropores.²⁸ This competition shows that the autoinhibition of arene acetylation, that is, the inhibition by the acetylated products, and also by the very polar acetic acid product is generally observed. This effect is much more pronounced with hydrophobic substrates such as methyl and fluoro aromatics than with hydrophilic substrates because of the larger difference in polarities between substrate and product molecules.

Various solutions to limit the negative effect of the polarity of the acetylated products were proposed:

- Choice of operating conditions favoring the adsorption of the reactant molecules and the desorption of the product molecules; fixed-bed reactor instead of batch reactor, high molar substrate/acetylating agent ratio, low conversion, high temperature, use of solvents with adequate polarities.



Yield/ArH	AlCl₃	HBEA
	95 %	95 %
Chemical + Physical Steps	8	2
Aqueous effluents (t/t anisole)	4.5	0.035
Effluent composition (wt %)		
H ₂ O	68.7	99
Al ³⁺	5	0
Cl ⁻	24	0
Organics	2.3	1

Figure 12.7 Acetylation of anisole. Characteristics of the old (AlCl₃) and new (HBEA) technologies.

- Adequate choice and adjustment of the zeolite characteristics, small path of diffusion (small crystallites, mesopores), good balance between hydrophobicity and acidity.

Industrial processes were developed by Rhodia³³ for the selective acetylation of anisole into 4-methylacetophenone and veratrole into 3,4-dimethoxyacetophenone, which are, respectively, precursors of Parsol, used for sun protection, and of Verbutin, a synergist for insecticides. In both cases, the substitution of the new technology (fixed-bed reactor, HBEA or HFAU zeolites as catalysts, acetic anhydride as acylating agent) for the old technology (batch reactor, AlCl₃ as catalyst, and acetylchloride as acylating agent) constitutes a major environmental and economical breakthrough. The main improvements brought about by the new process of anisole acetylation are presented in Figure 12.7: this process is much simple, the consumption of water much smaller, and lower amounts of organic compounds and no mineral compounds in the aqueous effluents.²⁸

12.2.3.2 One-Pot Multistep Synthesis of Ketones on Bifunctional Zeolite Catalysts. One-pot multistep reactions constitute an elegant and efficient way to decrease the number of chemical and separation steps, hence, to develop greener synthesis processes. Bifunctional metal–acidic or metal–basic zeolite catalysts, which can be prepared easily with the desired properties (e.g., distribution of the

different types of active sites, characteristics of the diffusion path) are good candidates for these reactions.

A widely studied example is the synthesis of various ketones or aldehydes, such as methylisobutylketone from acetone, cyclohexylcyclohexanone from cyclohexanone, 1,3-diphenylbutan-1-one from acetophenone, 2-ethylhexanal from *n*-butyraldehyde. Thus methyl isobutyl ketone (MIBK), which is used as a solvent for ink and lacquers, was previously prepared through the three-step catalytic process: base catalyzed production of diacetone alcohol (DA) by acetone aldolization, acid dehydration of DA into mesityl oxide (MO), then hydrogenation of MO on a Pd catalyst (Figure 12.8). Since acetone aldolization also occurs by acid catalysis, it is possible to synthesize MIBK in one apparent step by combining the acidic and hydrogenation functions. Most of the studies were carried out in the gas phase by using fixed-bed reactors.

The best yield and selectivity to MIBK were obtained with PdMFI:³⁴ 28 and 98% at 453 K or PdCsMFI:³⁵ 35 and 82%. Pd supported over large pore zeolites such as HFAU are much less selective. The main by-products are propane and 2-methylpentane resulting from three-step bifunctional catalytic transformations of acetone and methylisobutylketone, respectively (C=O hydrogenation, dehydration, and C=C hydrogenation).³⁶ This is why Pd, which is known to be more selective for the desired hydrogenation of the C=C bond than for the hydrogenation of the C=O bond, is generally chosen. Diisobutyl ketone (DIBK) may also be formed from acetone and MIBK through a bifunctional scheme similar to the one involved in MIBK formation.³⁶ The significance of the secondary reactions of MIBK (methylpentane and DIBK formation) can be significantly reduced by an adequate choice of the zeolite pore structure (preferentially tridimensional, to facilitate the desorption of MIBK) and of the crystallite size.

Pd supported over large-pore tridimensional acidic zeolites such as HFAU are the more active and selective catalysts for the synthesis of bulkier ketones. Thus, in a 0.2% Pd-HFAU catalyst, yield and selectivity from cyclohexanone of 23 and 75% can be obtained in cyclohexylcyclohexanone synthesis.³⁷ Furthermore, the synthesis of aldehydes can only be made selective by joining the hydrogenating metallic sites (Pd) to basic sites (instead of acidic sites). Thus, 2-ethylhexanal, which is a component of perfumes and fragrances, can be synthesized with high yield and selectivity (64 and 91%, respectively) on a PdKX zeolite.³⁸ Much lower yields and selectivities are obtained over nonzeolitic materials, such as Pd/MgO.

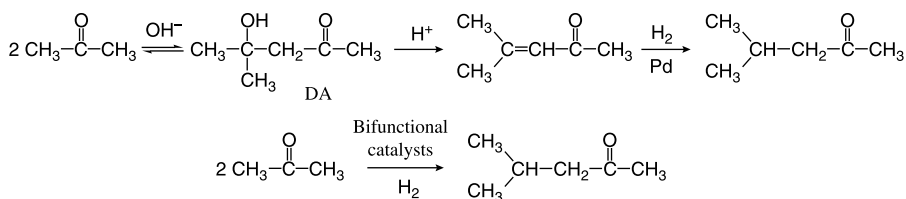


Figure 12.8 Synthesis of methyl isobutyl ketone (MIBK) from acetone.

12.3 CONCLUSIONS

As was shown here in some examples, the field of catalysis over zeolites, although mature, is still very much alive. The chemists who work with the synthesis of zeolites continue to be very creative, the focus now being placed on the synthesis of materials that can catalyze reactions other than the acidic ones and/or reactions of bulkier molecules, that is, synthesis of zeolites with larger micropores or with a very large external surface, such as nanosize and delaminated³⁹ zeolites. New concepts related to the mode of action of zeolite catalysts continue to emerge, as shown here with the shape selectivity of the external surface. These concepts are particularly useful to scientifically design selective and stable catalysts.

Since zeolite catalysts are successfully introduced in the refining and petrochemical industries, it is not surprising that most of the recent advances concern incremental improvements of existing processes with the development of new generations of catalysts (e.g., dewaxing, ethylbenzene and cumene synthesis). The number of newer applications is much more limited, for example, direct synthesis of phenol from benzene and aromatization of short-chain alkanes, etc. However, both the improvement and development of processes contribute significantly to environmental advances.

In the field of fine chemical synthesis there is an urgent need to substitute the cleaner technologies for the old polluting ones. It is hoped that the large economic and environmental benefits brought by the recently developed catalysis processes—acetylation of anisole and of veratrole, Beckmann rearrangement, and so forth—will initiate great strides in this field.

REFERENCES

1. Crönstedt, A. F. *Akad. Handl. Stockholm*, 1756, **18**, 120.
2. Maesen, T.; Marcus, B. *Stud. Surf. Sci. Catal.*, 2001, **135**, 1.
3. Guisnet, M.; Gilson, J. P. (Eds.) *Zeolites for Cleaner Technologies*, Imperial College Press, Singapore, 2002.
4. Weisz, P. B.; Frilette, V. J. *J. Phys. Chem.*, 1960, **64**, 382.
5. Baerlocher, Ch.; Meier, W. M.; Olson, D. H. (Eds.) *Atlas of Zeolite Framework Types*, 5th Rev. Ed. Elsevier, Amsterdam, 2001.
6. Barthomeuf, D. *Mater. Chem. Phys.*, 1987, **17**, 49.
7. Mirodatos, C.; Barthomeuf, D. *J. Chem. Soc. Chem. Commun.*, 1981, **39**.
8. Weisz, P. B. *Adv. Catal.*, 1962, **13**, 137.
9. Guisnet, M.; Alvarez, F.; Giannetto, G.; Perot, G. *Catal. Today*, 1987, **1**, 415.
10. Guisnet, M. *Pol. J. Chem.*, 2003, **77**, 637.
11. Chen, N. Y.; Garwood, W. E.; Dwyer, F. G. (Eds.) *Shape Selective Catalysis in Industrial Applications*. Chemical Industries 36, Marcel Dekker, New York, 1989.
12. Song, C.; Garces, J. M.; Sugi, Y. (Eds.) *Shape Selective Catalysis*, Am. Chem. Soc. Symp. Ser., vol. 738, 2000.

13. Degnan, T. F. Jr. *J. Catal.*, 2003, **216**, 32.
14. Derouane, E. G. *J. Mol. Catal. A: Chem.*, 1998, **134**, 29.
15. Daage, M. in *Zeolites for Cleaner Technologies*, Guisnet, M.; Gilson, J. P. (Eds.) Imperial College Press, Singapore, 2002, p. 167.
16. Alvarez, F.; Ribeiro, F. R.; Perot, G.; et al. *J. Catal.*, 1996, **162**, 179.
17. Martens, J. A.; Souverijns, W.; Verreslt, W.; et al. *Angew. Chem. Int. Ed.*, 1995, **34**, 2528.
18. Martens, J. A.; Parton, R.; Uytterhoeven, L.; Jacobs, P. A. *Appl. Catal.*, 1991, **79**, 95.
19. Guisnet, M. *J. Mol. Catal. A: Chem.*, 2002, **183**, 367.
20. Beck, J. S.; Haag, W. O *Handbook of Heterogeneous Catalysis*, Ertl, G.; Knözinger, H.; Weitkamp, J. (Eds.) VCH, Weinheim, 1997, p. 2123.
21. Beck, J. S.; Dandekar, A. B.; Degnan, T. F. in *Zeolites for Cleaner Technologies*, Guisnet, M.; Gilson, J. P. (Eds.) Imperial College Press, Singapore, 2002, p. 223.
22. Leonowicz, M. E.; Lawton, S. L.; Partridge, R. D.; et al. *Science*, 1994, **264**, 1910.
23. Lawton, S. L.; Leonowicz, M. E.; Partridge, R. D.; et al. *Micropor. Mesopor. Mater.*, 1998, **23**, 109.
24. Laforge, S.; Martin, D.; Guisnet, M. *Appl. Catal A: Gen.*, 2004, **268**, 33.
25. Du, H.; Olson, D. H. *J. Phys. Chem. B*, 2002, **106**, 395.
26. Rigoreau, J.; Laforge, S.; Gnep, N. S.; Guisnet, M. *J. Catal.*, 2005, **236**, 45.
27. Sheldon, R. A. *Chemtech*, 1994, **38**.
28. Marion, P.; Jacquot, R.; Ratton, S.; Guisnet, M. *Zeolites for Cleaner Technologies*, Guisnet, M.; Gilson, J. P. (Eds.) Imperial College Press, Singapore, 2002, p. 281.
29. Guidotti, M.; Canaff, C.; Coustard, J. M.; et al. *J. Catal.*, 2005, **230**, 375.
30. Berreghis, A.; Ayrault, P.; Fromentin, E.; Guisnet, M. *Catal. Lett.*, 2000, **68**, 121.
31. Fromentin, E.; Coustard, J. M.; Guisnet, M. *J. Catal.*, 2000, **190**, 433.
32. Moreau, V.; Fromentin, E.; Magnoux, P.; Guisnet, M. *Stud. Surf. Sci. Catal.*, 2001, **135**, 4113.
33. Spagnol, M.; Gilbert, L.; Benazzi, E.; Marcilly, C. European Patent WO9635655 (1996) (Patent to Rhodia).
34. Huang, T. J.; Haag, W. O. U.S. Patent 4,339,606 (1982) (Patent to Mobil Oil Corp.).
35. Chen, P.Y.; Chu, S. J.; Chang, N. S.; et al. *Stud. Surf. Sci. Catal.*, 1984, **46**, 231.
36. Melo, L.; Giannetto, G.; Alvarez, F.; et al. *Catal. Lett.*, 1997, **44**, 201.
37. Alvarez, F.; Silva, A. I.; Ramoa Ribeiro, F.; et al. *Stud. Surf. Sci. Catal.*, 1997, **108**, 609.
38. Ko, A. N.; Hu, C. H.; Chen, J. Y. *Appl. Catal. A: Gen.*, 1999, **184**, 211.
39. Corma, A.; Fornes, V. *Stud. Surf. Sci. Catal.*, 2001, **135**, 73.