Review

Structure–activity relationship in zeolites

F. Ramôa Ribeiro *, F. Alvarez, C. Henriques, F. Lemos, J.M. Lopes, M.F. Ribeiro

Centro de Engenharia Biológica e Química, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

Abstract

In this review we will try to give an integrated view of the relation between the structure and the catalytic behaviour of zeolitic materials, covering both the compositional and the structural aspects. Due to the amount of work that has been done in this wide area of zeolite catalysis this will, necessarily, be an incomplete although, hopefully, unbiased work.

The paper will refer, not only to the relation that can be observed with natural and as-synthesised zeolites, but also to the wide range of techniques that are currently available for the 'tuning' of the catalytic properties of zeolitic materials. A special emphasis will be placed in all the aspects concerning shape selective catalysis, which is certainly the most striking form of a structure–activity relationship in heterogeneous catalysis.

Keywords: Microporous materials; Structure–activity relationship; Zeolites

1. Introduction

Zeolite and zeolite-related materials assume a very important role in the heterogeneous catalysis field and have seen a significant increase in the available range of catalysts in the last few years.

The interest in zeolitic catalysts arises from their unique properties, namely:

(i) their unique microporous structure which allows them to have the well-known molecular sieving behaviour that justifies their use in a wider field than catalysis and that makes their activity related to both the composition and the geometry of the structure;

(ii) the large number of available structures, ranging from the very narrow pore systems to those having pores large enough to process heavy molecules;

(iii) the possibility to control, in a variety of ways, not only the geometry of the structure but also its composition in a relatively wide range. This feature assumes a particular importance in the area of catalysis where zeolites have the largest impact – acid catalysis;

(iv) the capability of zeolites to act as hosts for a variety of guests with catalytically attractive properties, such as transition metal ions, small metal clusters or transition metal complexes.

In this review paper we will try to give an integrated view of the structure–activity relations in zeolites. This view will be given in the widest form possible, including both the geometrical and compositional influences on activity.

We will also review the main methods available at the present date to alter the various structural

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* Corresponding author.

parameters in zeolitic catalysts and analyse the influence that each of them appears to have in the activity of these solids.

2. Zeolite structures

For a long time zeolites have been described as crystalline silicoaluminates of very porous structure. However, recently, the type of structures that was typical of the silicoaluminates called zeolites has been obtained in a wide range of materials with chemical composition considerably different from these. The synthesis of AlPO materials, solids that contain aluminium and phosphorous instead of aluminium and silicon was just the tip of the iceberg, and by now many elements have been successfully incorporated into zeolite-type structures.

Although the different compositions confer on these materials widely different properties, both as catalysts and as adsorbents, we will indistinctly call *zeolites* all those materials sharing with the *original zeolites* the crystalline microporous structure.

One of the most striking features of the porous structure of zeolitic materials is that pore openings are of molecular dimensions (see Fig. 1), situated in the range that adsorption scientists would label as ultra-micropores, leading to the widely used

designation of *molecular sieves*. This characteristic has driven a great number of their applications, and will also be emphasised in this review for its implications on the structure–activity relations in zeolite catalysis.

A second interesting feature is the versatility of the structures themselves. In fact, a large number of modification procedures is currently available, ranging from ion exchange to hydrothermal treatments or chemical vapour deposition (CVD), that permits the tailoring of the various properties of the zeolite to the particular application that is envisioned.

3. Composition

The composition of the structure is one of the most important aspects that has to be taken into account when considering zeolite catalysis. In their major application, catalytic cracking, the possibility to regulate the activity and other parameters, namely through the acidity of the structure, is of paramount importance. In fact, the possibility of designing the acid–base properties constitutes a fundamental feature leading to the broad range of catalytic applications, mainly in petroleum industry [1,2], but also in organic chemistry [3,4].
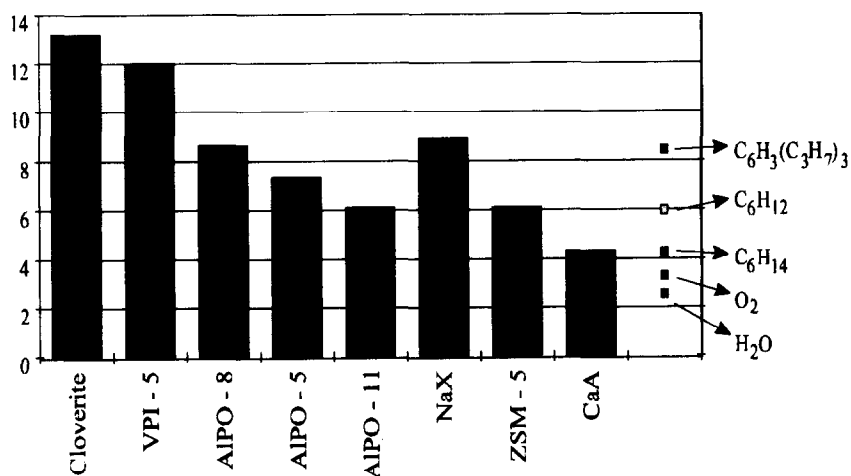

Fig. 1. Dimensions (in Å) of the pores of several zeolitic structures and some representative molecules.

Composition can be altered in many ways, including the incorporation of new elements into the zeolite structure [5].

3.1. Acidity in zeolites

Acidity can be introduced into a zeolite by a number of different ways, and can be achieved due to the particular charge balance of zeolitic frameworks. The existence of aluminium in a tetrahedrally coordinated silicon structure requires the existence of compensating cations that are located in the porous system of the structure. These cations are accessible for ion exchange, and, thus, acidity can be achieved by:

(i)   ion exchange with NH_4^+, followed by thermal decomposition;

(ii)   hydrolysis of ion-exchanged polyvalent cations;

(iii) reduction of exchanged metal ions to a lower valence state.

In all the examples above, Brønsted acid sites are formed. These sites can be further involved in dehydroxylation reactions, to form Lewis acid sites, under thermal treatments at temperatures usually in excess of 500°C [6].

The acidic catalytic properties of zeolites have been extensively used in many commercial processes. X, Y, Mordenite, L, and pentasil high-silica zeolites (ZSM-5, ZSM-8 and ZSM-11) are commonly used.

The hydroxyl groups with very acidic hydrogens have been recognised as the main source of these properties, especially of the efficient carboniogenic activity of zeolites [7,8]. Several parameters have to be taken into account to evaluate the acidity of a zeolite in relation to a particular application. Besides the structure, other parameters such as the total number of Brønsted and Lewis sites, their strength distributions and their location, have a significant influence on the effective acidity of any particular acid site in relation to a particular reaction.

At the same Al content, the strength of the Brønsted sites for several zeolites [9], and the

corresponding activities for *o*-dichlorobenzene isomerisation [10], follows the order HZSM-5 > HM > HBeta > HOff, showing the influence of the structural factors. Another example is the catalytic ability of faujasitic zeolites and ZSM-5, with similar compositions, which may differ by two orders of magnitude on the n-hexane cracking [11]. Similar observations, of purely structural factors influencing catalytic activity, have been made when comparing Y zeolite with ZSM-20 [12,13].

Choudhary [14] compared the acidity/site energy distributions in some catalytically important zeolites, and found the following order, if the zeolites were arranged according to the amount of strong acid sites:

$$HY \approx HM > CeNaX > CeNaY > HZSM-8$$

$$> HZSM-5 > HKL \gg HZSM-11$$
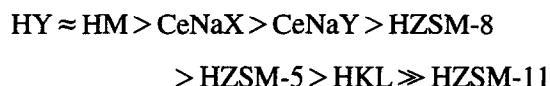
The catalytic activities per strong acid site, as well as the acidity of the Brønsted sites was shown to depend strongly on both the structure and the topology of the zeolite, and the chemical composition of its environment [15] (see Fig. 2), in particular on the Si/Al ratio. This aspect still deserves considerable attention, and just recently Corma reported data concerning the cracking of long chain alkyl aromatics over several zeolites [16] (see Fig. 3).
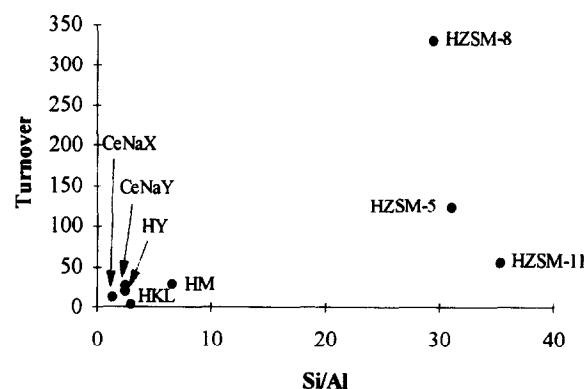

Fig. 2. Turnover number (molecules transformed per Al per second) for the conversion of cumene over various zeolites as a function of the Si/Al ratio (adapted from ref. [15]).
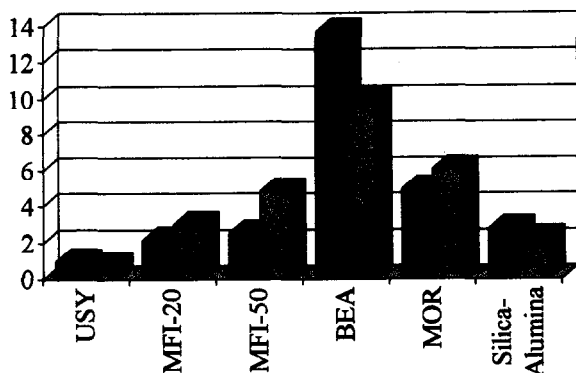
Fig. 3. Dealkylation/cracking (dark shading) and olefin/paraffin (light shading) ratios for the transformation of long chain alkyl aromatics over different zeolites (adapted from ref. [16]).

There is usually an increase in the number of strong Brønsted acid sites when the Si/Al ratio is increased, despite the reduction of the total amount of sites [17]. Also, theoretical approaches, such as those using an electronegativity model for evaluating the charge on the hydrogen atoms in zeolites [18], or the study of proton affinity [11], or quantum chemical methods [19,20], confirmed this fact. The aluminium atoms induce a higher degree of electron donation than silicon, resulting in a higher oxygen charge and proton–oxygen interaction [21]. Consequently, the acid site strength is reduced as the number of the aluminium neighbours increases, and will be dependent on the Al ordering, for a given composition [17,22,23]. Many data for acid catalysed processes revealed a parallel trend with the aluminium framework content [17,24], for limited Si/Al ranges. Generally, the catalytic activity goes through a maximum under further Si/Al increases [10,17,25,26]. This optimum value depends on the framework density of the zeolite [9].

Some dealumination processes, commonly used, can originate the formation and deposition on the porous structure of cationic aluminium species, which can act as Lewis sites or poison the strongest acid sites [27,28]. The presence of Lewis acid sites also has some influence on the Brønsted acidity strength. The inductive effect associated with the Lewis sites on the neighbour-

ing protonic sites increases the latter's acid strength, resulting in an enhancement of some catalytic reactions [29,30].

One way to control the relative amount of protonic sites is the regulation of the extent of ion exchange achieved on the zeolite preparation. The resulting average acid strength also depends on the exchange level, because the different proton sites' locations are frequently not equivalent, and because the global inductive effect will be changed.

Several examples are known on how the activity of Y zeolites changes when the Na$^+$ exchange level is altered [31,32], and similar behaviour has already been observed in other zeolites, such as ZSM-20 [33] (see Fig. 4).

The effect of the nature of the compensating cation on the acid strength, although quite smaller than the framework composition, is not negligible. The exchange of protons by K$^+$ ions on Y zeolite brings a more significant acid strength decrease than the exchange by Na$^+$ cations [34]. Different changes in the charge on hydrogens are induced by these cations. For a given cation valence, this effect results from differences in cation size; for instance, for hydrocarbon cracking on faujasites, the order of the deactivating effect follows the order K$^+$ > Na$^+$ > Li$^+$ [35].

Among the studies on the influence of the compensating cations on the acidity and the catalytic activity, those related to the rare-earth cations,
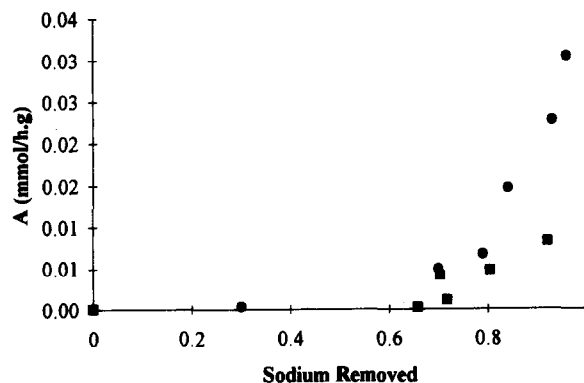

Fig. 4. Activity of HNaY (■) and HNaZSM-20 (●) for the cracking of n-heptane at 350°C as a function of the fraction of sodium substituted by protons (from refs. [32] and [33]).

especially on Y zeolite, have been particularly important considering the industrial applications [36].

The rare-earth exchanged Y zeolite shows improved catalytic properties on the cracking reactions, especially in respect to thermal stability. Several studies have shown that rare-earth cations, such as Ce^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, can induce a positive effect on the acidity and catalytic activity of faujasitic zeolites for hydrocarbon transformations [33,37–43]. This enhancement occurs since multivalent cations can hydrolyse the water molecules at temperatures near 300°C, generating Brønsted acidity [44,45] and producing an inductive effect on their closest protonic sites, increasing its acid strength; it is also important that a higher electric field gradient will favour the polarisation of the reactant molecules. This improvement is dependent on the cation exchange level, the cracking activity going in many cases through a maximum for an optimum rare-earth content, when the material to be exchanged presents already some Brønsted acidity.

The most important application of acid catalysis by zeolites concerns the transformation of hydrocarbons. This transformation over acidic zeolites shows a markedly different behaviour from that for non-acid zeolites [46]: the catalytic activity is much higher; skeletal isomerisation is observed and the product distribution is generally consistent with a carbenium ion formation at the acid sites, rather than free radical mechanism; extensive hydrogen transfer is normally achieved between naphthenes and olefins, forming paraffins and aromatics [47,48]. The reaction proceeds either by β-scission or by penta-coordinated carbonium ions [47,49,50], the latter mechanism being favoured by a higher field gradient, e.g., highly

constraining porosity, low aluminium content, and polarising cations [51,52].

Recently, the concept of soft–hard acidity was used to explain some differences in the selectivities, during several processes, as, for example, the alkylation of alkylaromatics by carbocations, not explainable on the basis of acid strength [53]. While the acid strength depends on both chemical composition and distribution on its surrounding, the hardness is mainly dependent on the composition. Once again the Si/Al ratio is important: the hardness of the acid zeolite increases with the aluminium content.

The average site density, or the so-called number of next nearest neighbours (NNN) appears to control the balance between monomolecular and bimolecular reactions [54,55]. Increasing the acid site density in faujasitic zeolites produces an enhancement of coke selectivity [56], which clearly expresses the increment on bimolecular processes, involved in coke formation, relative to unimolecular ones. In addition to this effect, the level of dealumination can modify the adsorption selectivity, or its surface hydrophilicity, which will be reflected on the balance just referred [25,57].

Theoretical calculations have shown that the average framework electronegativity depends on the framework density (number of Si per nm³) [58], the highest value coinciding with the most open structure of faujasitic zeolites. Typical values for the calculated electronegativities of several zeolites are presented on Table 1, where the comparison is made for pure silica zeolites.

3.2. Non-acidic effects

The effect of zeolites as electrolytes on catalysis, without contribution from acidic hydroxyl

Table 1
Framework densities, d, and average framework electronegativities, $\bar{\chi}$, for some zeolites [58]

Zeolite	M	ZSM-11	ZSM-5	ERI	OFF	L	CHA	A	FAU
χ (eV)	5.67	5.68	5.69	5.83	5.84	5.86	5.93	5.99	6.23
d (Si/nm³)	17.1	18.2	18.0	16.0	16.0	16.4	15.0	14.2	13.0

groups, can be observed, for example, by studying the hydrocarbon transformation on alkali zeolites [59,60]. Low silica zeolites concentrate hydrocarbon reactants within the intracrystalline surface due to high electrical fields inside the pores. This results in an enhancement of the rates of bimolecular reaction steps and stabilisation of ionic species, as observed, e.g., for KY zeolite, contrasting with silicalite, which is a very weak electrolyte.

Recently Espeel et al. [61] demonstrated the use of a zeolite as a 'solid solvent'. They showed that faujasite-type zeolites with specific Si/Al ratios exchanged with $Pd(NH_3)_4^{2+}$ and Cu^{2+}, catalysed the oxidation of ethylene to acetaldehyde in a manner similar to the homogeneous Wacker system, where the chloride ion is replaced by the anionic zeolitic framework.

The ion exchange and framework periodicity properties of zeolites enable functional metal ions or complexes to be stabilised in a variety of oxidation states and coordination geometries. Non-acid catalysis has been successfully achieved, namely for reactions such as oxidation, reduction, olefin oligomerisation, carbonylation, hydroformylation, synthesis gas conversion [62], bimolecular condensation of ethanol [63].

Zeolites can be used effectively on bifunctional catalysis when a metal function is generated alongside Brønsted acidity [64]. Polyfunctional catalysis have also been accomplished with zeolites doped with metals [65].

Exchanged transition metal ions can stabilise the zeolite framework, coordinate adsorbed molecules and/or act as independent catalytically active sites [66–69].

An important feature, that has recently received considerable research attention, is the ability of zeolite basic sites to catalyse some reactions [70–72]. Zeolites in the alkaline form, or containing metal clusters, can be used on base-catalysed reactions [63,73–75]. Some reactions seem to occur via carbanium intermediates [74], such as olefin isomerisation and oligomerisation [76].

The zeolite lattice oxygen ions constitute basic sites, as well as occluded alkali metal or alkali metal compounds [22,76]. The crystal structure,

framework composition and compensating ion, will also be determinant for the zeolite basicity. For example, a NaX zeolite presented higher catalytic activity than a NaY zeolite on the base-catalysed dehydrogenation of isopropyl alcohol [77]. By exchanging Na^+ into K^+, Rb^+, Cs^+, this reaction is strongly enhanced, while Li^+ cation induces its depression. The effect of these cations on the basicity strength follows the same order [78].

The basic strength of the framework oxygen, and consequently, some of the catalytic properties of the alkali-metal exchanged zeolites, was proposed to be rationalised in terms of the electronic structure characterised by XPS [79]. The average framework electronegativity is also an important parameter expressing the zeolite basicity [80].

The concept of surface curvature effect has also been proposed as constituting a geometrical contribution to the specific activity of an active site [81], and which may be important even on large pore zeolites.

3.3. Hydrophilicity/hydrophobicity

The intracrystalline pore–cavity system, which constitutes the zeolitic surface, is strongly influenced by the zeolite's crystal field, rendering zeolites as solid electrolytes, as already mentioned above. The aluminium content is the main parameter determining the ionic character of the crystal, and consequently it regulates the polar properties of the zeolite, its strength as an electrolyte increasing with aluminium content. The polar character of some zeolite surfaces will produce a strong interaction with polar and polarizable molecules.

The surface selectivity, highly hydrophilic in the low silica zeolites, becomes hydrophobic in the high silica ones [82]. Zeolites A and X are aluminium rich, thus presenting the highest cation concentration, and consequently a highly heterogeneous surface, from the point of view of electrical charges, with a strongly hydrophilic surface selectivity. Examples of intermediate Si/Al zeolites ($2 < Si/Al < 5$) are erionite, chabazite, mor-

denite, Y, omega and L, which still present hydrophilic surface character. The high silica zeolites $(10 < Si/Al < 100)$, which can be prepared by framework modification of hydrophilic zeolites, as the siliceous variants of Y, mordenite, etc., or by direct synthesis, as the zeolite beta, ZSM-5, -11, -12, -21, -34, etc., are reported to be hydrophobic. The equilibrium adsorption isotherms for water, oxygen and n-hexane on some of these zeolites [82], is reported to illustrate these differences in surface selectivity. Another example is that a progressive increase of Si/Al ratio can improve the ethanol/water separation [83].

Low and intermediate silica zeolites are able to remove water from organics and can be used in catalysis on dry streams. Hydrophobic zeolites can remove organics from water streams and participate in catalytic processes in the presence of water. The hydrophobic or hydrophilic character of the zeolite can influence the activity of catalytic processes involving water, such as carboxylic acid esterification or ethylenic hydrocarbon hydration [3].

However, it is not possible to distinguish the influence of hydrophobicity/hydrophilicity from the acidity effects, both being closely connected [84].

3.4. Non-classical framework compositions

The introduction into the framework of atoms other than Si and Al can modify significantly the acid–base and catalytic properties of the zeolites. It is also possible to obtain useful materials for new catalytic processes [85,86].

Some modification studies have been made with framework gallium insertion, substituting aluminium on the synthesis process [87–91]. These modified materials are interesting for the aromatisation of light alkanes [89]. The presence of gallium on the X and high silica zeolite's frameworks induces an increase in the selectivity for aromatisation on the reaction of alcohol dehydration [92].

NaX zeolite, in which the silicon has been substituted by Ge, was shown to be much more active on the basic catalysed benzaldehyde condensation reaction than the classical aluminosilicate form [93]. In this case, not only the electronegativity has to be taken into account, but also the T–O–T angle change. The alumogermanate form of X as well as high silica zeolites revealed high selectivity for propylene on the alcohol dehydration process [92]. Other possibilities are also the incorporation of B and Fe into the framework.

The hydroxyl acid strength, evaluated by infrared spectroscopy and temperature programmed desorption of bases, suggests the following order [94,95]: $Si(OH) < B(OH)Si \ll Fe(OH)Si < Ga(OH)Si < Al(OH)Si$.

The borosilicate analogue of ZSM-5 is an active, shape-selective, acid catalyst, much like ZSM-5 itself, while gallosilicate is used in the Cyclar process, from BP, where propane and butane are aromatized [95].

Also titanosilicates have been found to be of importance in oxidation catalysis [95,96]. The titanium silicalite is an industrial catalyst for the epoxidation of olefins [95].

Several years ago, the families of phosphorus-containing zeolites, known as ALPO-n (aluminophosphates) and SAPO-n (silicoaluminophosphates) were reported [97]. Many different structures have been obtained, some of them new ones, and many others topological analogues of aluminosilicate zeolites. These microporous solids exhibit properties characteristic of known aluminosilicates and show some physicochemical traits as a consequence of their unique chemical composition [98,99].

ALPO-n materials consist of alternating aluminium(III) and phosphorus(V) tetrahedra, such that Al/P = 1, forming a neutral framework [100].

In the SAPO-n family, some silicon substitutes phosphorus and/or pairs of aluminium–phosphorus. The substitution mechanism may vary from structure to structure, and is responsible for the generation of surface acidity [97,100–103]. Their acid–base properties show a complex dependence on the structure type, composition and charge of the framework [101].

Applications of these acidic properties have been reported on methanol conversion to alkenes [104–107], improving the selectivity relative to ZSM-5 and erionite–offretite zeolites, as well as in some general rearrangement reactions of alkenes, alkanes and aromatics [108]. Bifunctional catalytic applications were also reported on metal-loaded SAPO materials [109–111]. Usually, they present weak to mild acidic properties relative to the correspondent aluminosilicates [112–114], especially when tested on demanding reactions, such as hydrocarbon conversion. Silicon content is a major parameter influencing the number and strength of the acid sites [115], as well as the framework atom ordering and homogeneity [115–119].

Many ALPO-based molecular sieves have been prepared through the incorporation on its framework of several metals, as Co, Mn, Mg, B, Ti, Fe, Zn, Ga, Ge and As, resulting in some particular catalytic properties [82,120–122]. The substitution of divalent cations for the Al(III) framework species generates a negative lattice charge, and so Brønsted acidity. The same type of substitution has been reported on silicoaluminophosphates [82,110,123].

4. Geometry

Zeolitic materials possess a well-defined pore structure within which is confined the major amount of active sites. Access to the cavities of zeolites is possible through voids of various sizes which are of a size comparable to that of small molecules; Fig. 1 shows some typical zeolite pore sizes compared to the diameter of various molecules [124]. Their catalytic activity is remarkably affected by this unique geometrical property, and one of the most striking effects that can be observed is shape selective catalysis.

Although its influence is not particularly important in catalytic cracking, the most important process using zeolitic acid properties, it is a major factor in other applications of zeolites and of par-

amount importance in processes such as *methanol to gasoline* and *xylene isomerisation*.

4.1. Shape selectivity

The term 'shape-selective catalysis' was proposed by Weisz and Frilette in 1960 [125] and refers to the fact that zeolites can be shape and size selective in catalytic molecular rearrangements. These authors found that the small pore zeolite A, exchanged with calcium, selectively cracked straight chain paraffins to straight chain products. Other examples on shape-selective catalysis with small and large pore zeolites soon followed [126–130]. This new aspect of zeolite catalysis is, perhaps, the most striking example of structure–activity relationship.

Over the past years many new zeolitic materials have been discovered. Of particular importance was the discovery of the synthetic medium pore zeolites with 'port' sizes of 5 to 6 Å, especially of ZSM-5 [129]. One of the unique shape-selective characteristics of ZSM-5 is its *para*-selectivity in electrophilic substitution reactions, such as alkylation and disproportionation of alkyl aromatics.

ZSM-5 is remarkably stable as an acid catalyst. This is probably due to its peculiar structure with 10-membered oxygen-ring-sized pores of uniform dimension and absence of large supercages with smaller size windows [130]. These geometrical factors impose geometrical constraints on the formation of large polynuclear hydrocarbons responsible for coking [131–133]. The combination of acidity, shape selectivity and low coke formation are responsible for the successful industrial applications of ZSM-5 based zeolites [1,2,134], such as: manufacture of petrochemicals (ethylbenzene and *p*-xylene), M-forming process for octane improvement of reformate gasoline, dewaxing of middle distillates and lubricating oils and production of gasoline from methanol. HZSM-5 is also used as an additive in some FCC catalysts for octane enhancement of gasoline. Another commercial shape-selective process, Mobil's Selectoforming, uses an erionite based catalyst [127].

Since shape-selectivity is a geometrical property, it is not restricted to acid catalysis. In fact, it has been observed that zeolites in their alkaline form can be used in shape-selective base catalysis [77]. In addition, zeolite structures can accommodate small metal particles and perform metal catalysis or bifunctional catalysis, thus giving a much wider range to the possible applications of this important feature.

In recent years numerous potential applications of shape selectivity of zeolites have also been found in the synthesis of organic intermediates and fine chemicals [3,134–136]. However, because of the greater polarity of organic substrates containing heteroatoms, relative to the hydrocarbons that constitute the 'classical' substrates in zeolite catalysed reactions, shape selectivity effects are in some cases superimposed on electronic factors [137].

4.1.1. Generalities on shape-selective catalysis

A number of comprehensive reviews and critical discussions on the principles and applications of shape-selective catalysis [128,134,138–142] have been published by several authors.

The concept of molecular shape-selective catalysis implies an intimate interaction between the shape, size, and configuration of reactants, transition states and products, and the dimensions, geometry and tortuosity of the channels and cages of the zeolite [141].

Csicsery has categorised the following three shape selective effects:

Reactant selectivity, which takes place when some molecules of the feed are too bulky to diffuse through the zeolite pores and are prevented to react. An example is Mobil's Selectoforming process where linear paraffins are selectively hydrocracked from a mixture of paraffinic and aromatic hydrocarbons over an erionite based catalyst [127]. Branched and cycloparaffins and aromatic hydrocarbons are not affected (see Fig. 5).

Product selectivity, which occurs when similar restrictions apply to the product molecule (see Fig. 5). It plays an important role in the selective production of *para*-aromatic compounds on ZSM-

5 based catalysts [130] and also affects the deactivation by coking of catalysts in general [132,133].

Restricted transition-state selectivity, which occurs when certain reactions are prevented because some transition state in the reaction pathway (bimolecular, for example), requires more space than that available in the intracrystalline void volume. The near-absence of transalkylation in the isomerisation of the xylenes on ZSM-5 catalysts was justified by the restrictions imposed by the zeolitic structure to the formation of bimolecular complexes [143]. Related to this type of shape-selectivity is the so-called restricted growth type selectivity [137] in which the formation of higher addition, substitution or oligomerisation products is suppressed due to the geometric dimensions of the products.

Reactant and product selectivity are the ways of achieving molecular shape selectivity by size exclusion. In the present literature there are, however other expressions for less direct manifestations of molecular shape-selectivity:

Concentration effect, which was proposed by Rabo [144] and refers to the increased concentration of hydrocarbons in zeolites, thus favouring bimolecular over monomolecular reactions. A special case of this effect is the so-called cage effect, which is present in zeolites with erionite cages (erionite, T zeolite). In these zeolites the mobility of molecules such as n-heptane and n-octane is strongly reduced because they fit perfectly into the erionite cage. Therefore their diffusivity is minimum whereas their reactivity is maximum.

Molecular traffic control: this concept was proposed by Derouane and Gabelica [145] to explain the unusual absence of counter-diffusion effects in the ZSM-5 catalysed conversion of methanol to hydrocarbons. According to the concept, the smaller molecules enter the sinusoidal channels while the larger product molecules exit from the elliptical channels. However the same authors [146] have shown that the catalytic behaviour of zeolite ZSM-11, which has intersecting straight channels of the same size, was very similar to that
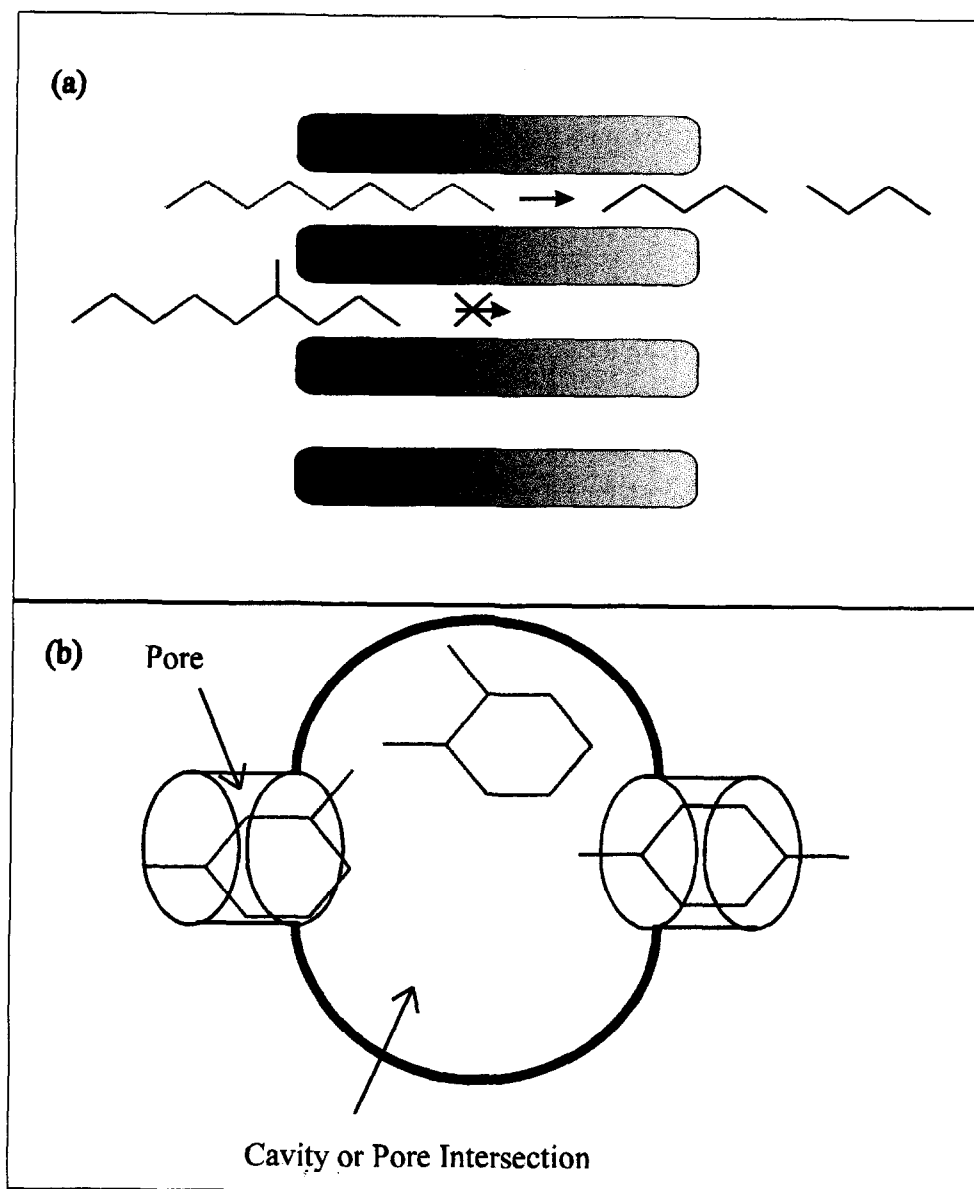
Fig. 5. Schematic representation of the shape selectivity effects due to (a) reactant and (b) product size exclusion.

observed with ZSM-5 for reactions such as the transformation of methanol to hydrocarbons and the alkylation of toluene with methanol indicating that this effect is of minor importance.

Molecular circulation, which determines the way in which molecules approach pore mouths and which was found in dual pore zeolites such as offretite [147].

Energy gradient selectivity [148]: this effect explains the occurrence of secondary reactions when hydrocarbons are cracked in a tortuous environment; it also takes into account differences in the field gradient caused by isomorphic substitution.

4.1.2. Diffusional effects

The factors which govern intracrystalline diffusion are very important for the discussion of molecular sieve catalysts. Zeolites present a particular kind of diffusion, which deviates from the

classical molecular and Knudsen diffusion regimes, precisely because of the similitude of sizes between the molecules and the pores of the catalysts. This diffusion regime was named by Weisz as configurational diffusion [149]. A unique feature of this diffusion regime is that very small changes in the molecule to pore sizes relationship induce very large changes in the diffusion coefficient. This is one of the fundamental effects that gives rise to shape selectivity. For example, the hydrogenation of *trans*-butene-2 over Pt/zeolite A was found to be much faster than that of *cis*-butene-2 [150]. In fact, although the size difference between the *cis*- and *trans*-isomers is only of 2 Å, the diffusivity of *trans*-butene-2 is at least 200 times greater than that of *cis*-butene-2.

Another example of this configurational diffusion effect is the achievement of *para*-directed aromatics in alkylation and toluene disproportionation reactions [130]. The increase of crystallite size of ZSM-5 leads to an increase in the diffusional constraints imposed to the bulkier *ortho*- and *meta*-isomers. The production of those isomers is then reduced and the yield of *para*-isomer is increased [151].

4.1.3. Size exclusion

As the size of the molecules increases (or the pore size decreases) there comes a time when the molecules can no longer penetrate the pore system of the zeolite. This leads to molecular shape selectivity by size exclusion and can also be achieved through either reactant selectivity or product selectivity. The separation of molecules of different sizes and shapes can be performed by the proper choice of zeolite (Fig. 1). The effective size of the pores can be further modified by several methods, which will be discussed further on. Some examples of reactant selectivity, besides those already given are the selective dehydration over CaA of n-butanol in a mixture of n-butanol and isobutanol [126], and the selective cracking of n-hexane in the presence of 3-methylpentane over small pore zeolites [152].

The product selectivity by size exclusion was demonstrated by Weisz et al. [126] by the absence

Table 2
Monobranched/multibranched ratio (M/B) and yield of trimethylbutane (TMB) from n-heptane on Pt–zeolites at the maximum isomerisation conversion [154]

Zeolite	Pore dimensions (Å)	M/B	TMB (%)
USHY	0.74	3	4
Offretite	0.67; 0.36×0.49	3.4	1.3
ZSM-5	0.53×0.56; 0.56×0.65	12	0

of branched chain products (isobutane and isopentane) resulting from the cracking of n-hexane on CaA zeolites. Another example was found in the conversion of methanol to hydrocarbons over ZSM-5, where hexamethylbenzene is not formed, in spite of the importance of the reaction of methylation of the aromatic ring [153].

In the hydroisomerisation of n-paraffins size exclusion of products was also verified; Giannetto et al. [154] found in the hydroisomerisation of n-heptane over Pt–zeolites that the relative amount of dibranched isomers and of the tribranched trimethylbutane decreased with the pore size of the zeolite; the tribranched isomer was not found on PtHZSM-5 (see Table 2). A similar result was obtained by Jacobs et al. [155] in the hydroisomerisation of n-decane on PtHZSM-5: absence of tribranched isomers and less amount of dibranched isomers when compared with the large pore Y zeolite.

4.1.4. para-Selectivity

para-Selectivity deserves a special reference due to its importance in a series of industrially significant reactions. It is a form of selectivity that originates from one of the two effects discussed above (*diffusion effects* or *size exclusion*) and appears mainly in ZSM-5 based catalysts, which possess an unique shape-selective characteristic for the preferential formation of *para*-aromatic compounds. Molecules such as *para*-dialkylbenzenes diffuse much more rapidly into medium pore zeolites than their corresponding *ortho*- and *meta*-isomers. By adjustment of the acid activity of the zeolite and controlling the diffusion parameter, high *para*-selectivity can be achieved. A gen-

eral correlation [134] for good *para*-selectivity is that

$$\frac{1}{k} \ll \frac{R^2}{D}$$

where k is the reaction rate constant, R is the crystal radius and D is the diffusivity of the species with the slowest diffusion rate.

As will be shown later, without changing the intrinsic activity of the catalyst and the size of the crystal, the effective diffusion characteristics of the catalyst can be altered by several techniques. Diffusion/reaction interaction can explain the yields in *para*-isomers that sometimes even exceed the expected equilibrium conversion.

Countless papers on this subject have appeared. A few examples of *para*-selective reactions over ZSM-5 are: isomerisation of xylenes, the alkylation of toluene with methanol, the selective formation of *para*-ethyltoluene in the reaction of alkylation of toluene with ethene, and the preferential formation of *para*-cymene in the alkylation of toluene with propene [134,141].

Similar kinds of *para*-selective reactions with hydrocarbons containing heteroatoms over ZSM-5 based catalysts have been reported, e.g. in the alkylation of chlorobenzene with methanol [156], and the acylation of anisole by acyl chloride and carboxylic acids [157].

Recently *para*-selective effects have been reported in reactions catalysed by zeolites other than ZSM-5, namely the selective conversion of toluene to *para*-xylene on ZSM-23 and ZSM-48 [158,159], the exclusive formation of *para*-diethylbenzene from the alkylation of ethylbenzene on modified ZSM-5, ZSM-11 and ferrierite [160], and the preferential formation of *para*-dialkylaromatics when toluene is alkylated with methanol and ethylbenzene with ethanol on zeolite KZ-1 [161].

4.1.5. Restricted transition state molecular shape-selectivity

Restricted transition state molecular shape-selectivity is observed when steric constraints in the environment of the catalytic site affect or pre-

vent the formation of intermediate complex structures. This type of shape-selectivity is independent of crystal size and activity, but depends on pore and cavity diameters and on the zeolite's structure. Actually, most of the model reactions proposed to characterise the pore structure of zeolites, some of which will be discussed below, make use of the differences of transition states generated in different acid environments.

Restricted transition state molecular shape-selectivity was first proposed by Csicsery [162] to explain the absence of symmetrical trialkylbenzenes in the product from the disproportionation of a dialkylbenzene over H-mordenite. Since the reaction is bimolecular the diphenylmethane type intermediate must require more space than that available in the mordenite channels. The low xylene disproportionation activity of ZSM-5 was also explained by this type of shape-selectivity. The activity for this reaction on various zeolites (ZSM-5, ZSM-4, mordenite and Y zeolite) were correlated with their effective pore size [163,164]. As expected the transalkylation was dramatically inhibited as the pores became more restrained.

The high ethylbenzene selectivity which characterises the formation of ethylbenzene from benzene and ethene by the Mobil Badger process [165], is also due to restricted transition state molecular shape selectivity. ZSM-5 inhibits the formation of polyalkylated benzenes normally obtained with non-shape selective catalysts. As a consequence the process is more selective and the catalysts have a stable activity.

An interesting example of transition state molecular shape selectivity was recently reported by Martens et al. [166]. These authors have studied the ketonization of mixtures of low carbon number carboxylic acids over the H-T zeolite. It was found that this small pore zeolite is particularly suitable for converting an equimolar mixture of propionic and butyric acid in 3-hexanone. These acids seem to have the optimum size for a bimolecular ketonization reaction inside an erionite cage.
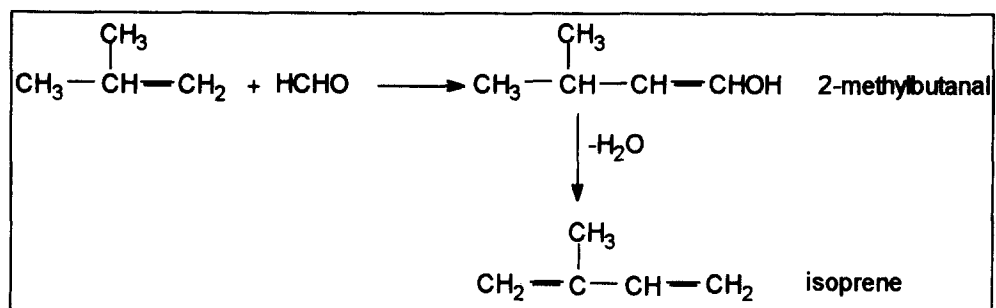
Fig. 6. Reactional route for the Prins condensation of formaldehyde and isobutene to give isoprene.

A close related effect can be found in the inhibition by shape selectivity of consecutive reactions. One of the most famous examples is the limitation to C_{10} aromatic hydrocarbons in the products of the ZSM-5 catalysed methanol to gasoline process [134,140]. In the field of the reactions of hydrocarbons containing heteroatoms such limitations can also be found [3,167], for example with the acid catalysed Prins reaction of condensation of formaldehyde and isobutene. This reaction is a good route for the synthesis of isoprene (Fig. 6).

Over medium pore zeolites the formation of bulkier cyclic condensation products such as 4,4-dimethyl-1,3-dioxane is inhibited, contrarily to what was found on non-shape selective catalysts [167].

Transition state shape selectivity is also found in the selective cracking of paraffins in medium pore zeolites. Actually, the traditional cracking sequences and reactivities of alkanes, which can be derived from classical carbenium ion chemistry, are changed in medium pore zeolites [8], i.e., the reaction rate increase with chain length is less than in absence of steric constraints and the reactivity decreases as the degree of branching increases, rather than the reverse as in the case of large pore zeolites. It seems that diffusional effects play a major role in the cracking of multi-branched paraffins [134]. Nevertheless the relative rate of cracking of normal and monomethyl substituted paraffins is governed by transition state selectivity. For example, n-hexane and 3-methylpentane are readily adsorbed by ZSM-5; however the rate of cracking of the branched molecule is slower than the one observed with the straight chain molecule. According to Haag et al. [168] this is due to the greater amount of space required by the bulkier 3-methylpentane molecule to form the reaction intermediate (Fig. 7). The definition of a constraint index (CI) [169] to characterise medium pore zeolites arises from this effect, as we will see further on. Frilette et al. [169] have shown that the CI of a given zeolite was inde-
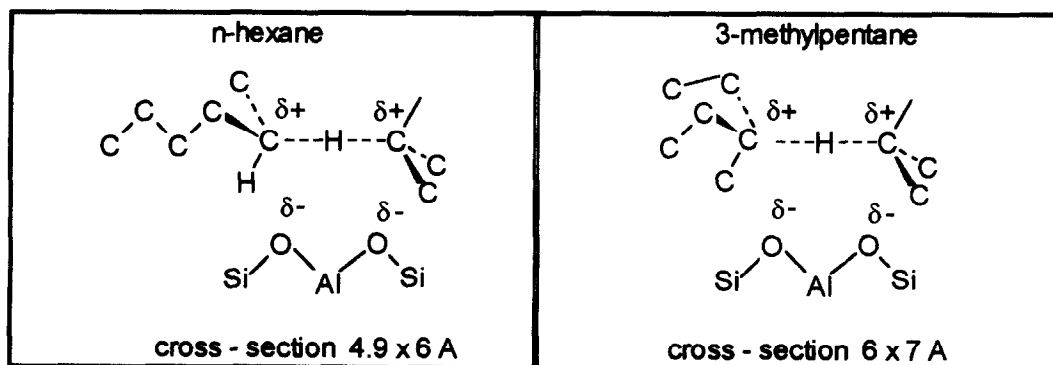

Fig. 7. Mechanism of paraffin cracking (adapted from ref. [56]).

pendent of crystallite size which proves that the observed cracking rate difference is not governed by diffusional effects.

The proposed interpretation is consistent with the classical mechanism of acid-catalysed paraffin cracking, involving bimolecular hydride transfer as the rate determining step. Nevertheless the temperature dependence of the CI [169], i.e. the fact that the constraint index of medium pore zeolites decreases with increasing temperature can only be explained by the participation of the monomolecular cracking mechanism [170], which involves the direct protonation of a paraffin molecule. The importance of the latter, less spatially constrained reaction increases with temperature, which can explain this temperature dependence of the CI of medium pore zeolites.

4.1.6. Metal catalysed shape selectivity

Zeolite structures can serve as hosts for small metal particles. The zero valent state of the metal (Pt, Pd, Rh...) is achieved by reduction after ionic exchange of metal salt into the zeolite. Inside the zeolitic structure the metal particles can perform shape selective hydrogenation and redox reactions. These shape selective reactions are of great importance in the field of fine chemicals.

In reactions that proceed through bifunctional catalysis, e.g. hydroisomerisation and hydrocracking of paraffins, metal centres (Pd, Pt) introduced in the zeolite by ionic exchange, act in conjunction with acid centres. Transition state shape selectivity effects, as seen above, occur also in this type of reaction, affecting the isomerisation to cracking rates ratio, the branched isomers distribution, and the cracking product distribution compared to what is found over large pore zeolites. In these reactions cracking follows isomerisation of the olefins generated on the metallic centres. It is well established that the methyl-branching of intermediate olefins occurs mainly through protonated cyclopropanes intermediates [171,172]. This mechanism predicts equal amounts of 2-methylnonane and 5-methylnonane and of 3- and 4-methylnonanes from decane [173,174]. Over Pt–Y zeolites the initial distri-

bution of methylnonanes is very close to that predicted [155,173–176] indicating that the micropore system of faujasite is not a shape selective environment with respect to methyl-branching of decane. In zeolites with smaller cavities and 10-membered ring ports, the formation of 2-methylnonane is favoured, mainly at the expense 4- and 5-methylnonanes [155,174]. A similar effect was found by Guisnet et al. [177] in the hydroisomerisation of n-heptane over PtZSM-5 catalysts; the kinetically unfavoured 2-methylhexane was formed at a rate about twice that of the formation of the 3-methylhexane isomer, in contrast to that observed in PtHY catalysts. Such observations have also been made by other authors [178].

Gallezot et al. [179] studied the selective hydrogenation of cinnamaldehyde in the liquid phase over a Pt-Y zeolite loaded with 14 wt.% of platinum, with platinum agglomerates of about 5 nm of diameter located inside the zeolite pores but near the external surface. The reaction scheme is given in Fig. 8.

The first hydrogenation step can lead to 3-phenylpropanal if hydrogenation takes place on the carbon–carbon double bond, or to cinnamyl alcohol if hydrogen adds to the carbon–oxygen double bond. A second hydrogenation step leads to 3-phenylpropanol. The authors found that hydrogenation on PtY catalyst gave much better selectivity to cinnamyl alcohol compared to a Pt/charcoal reference catalyst. The results were explained by shape selectivity effects: the geometric constraints in the pores impose an end-on adsorption of the reacting molecule over the metal, i.e. via its carbonyl group, and therefore a selective hydrogenation of the $C=O$ bond. The adsorption and activation of the central $C=C$ bond is strongly hindered due to the dimensions of the platinum clusters.

There are several examples of redox reactions performed with metal containing zeolitic structures [3,124,135–137]. In the oxidative acetoxylation of propylene to give allyl acetate, Pd/Cu–erionite, Pd/Cu–Mordenite and Pd/Cu–faujasite
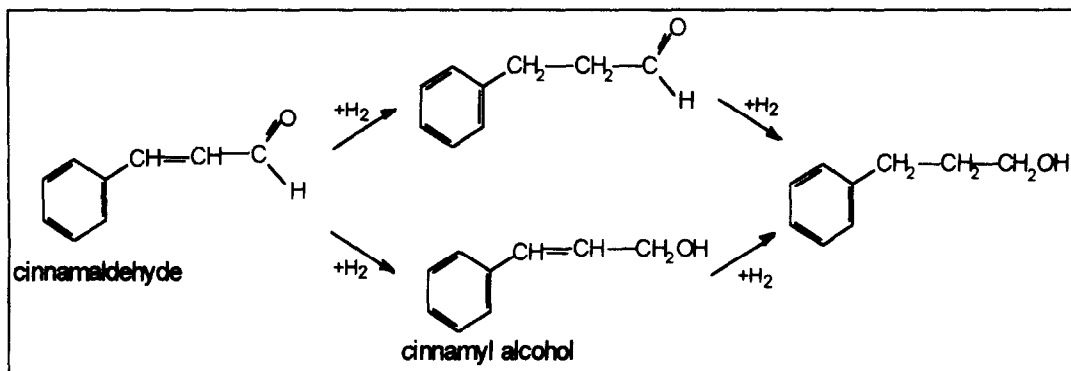
Fig. 8. Hydrogenation of cinnamaldeyde to cinnamyl alcohol (from ref. [67]).

give 90%, 70% and 40% selectivity, respectively [180].

The titanium substituted ZSM-5 (TS-1) is a metallosilicate possessing unique properties for the oxidation of organic substrates using H_2O_2 [181]. One result was the introduction in Italy of a new commercial process [181,182], the hydroxylation of phenol to hydroquinone/catechol mixtures. Recently [183], it was reported that the vanadium analogue of ZSM-11 (VS-2) is also a good catalyst for the same type of reactions. Titanium silicates are also good catalysts for other selective oxidation reactions with H_2O_2, e.g. olefin epoxidation [184] and oxidation of alkanes to a mixture of the corresponding alcohols and ketones [185,186]. The TS-1 catalyst is able to differentiate linear from branched and cyclic paraffins.

4.2. Pore size characterisation

For this particular property of zeolites to be fully exploited, reliable methods of pore system characterisation are needed. We can separate the methods currently used into two main groups: (i) those involving *physico-chemical measurements* and (ii) those involving *chemical reactivity measurements*.

4.2.1. Physico-chemical methods

Although these methods are somewhat outside the scope of this review, we think they should be briefly mentioned before embarking on our dis-

cussion of chemical reactivity measurements for pore size characterisation.

Classically, zeolite pore systems have been characterised by sorption of chemical species with different molecular dimensions, in order to obtain data on both size and volume of the voids within the crystal; oxygen sorption at 90 K seems to give a good estimate of pore volume and water sorption capacity [6,187]. The sorption of a range of hydrocarbons with different kinetic diameters, will also allow the determination of effective pore sizes within relatively narrow limits [188].

Precision X-ray diffraction (XRD) can be used to determine crystal symmetry, unit cell dimensions and space point groups [188,189]. Only when large single crystals are available (with a diameter of at least 40 μm), a combination of this method with model building, allows the calculation of atom coordinates [188] and thus obtain the complete solution of the structure of the crystalline solid [189,190]. Other techniques, such as diffraction of both electrons and X-ray, in combination with refinement procedures, can achieve structure solution of crystalline powders, in the 1 to 10 μm range [188,191,192]. Supplementary information on the presence of distinct crystallographic sites is available from MAS-NMR (magic angle spinning NMR). Reliable structural information, although only spatially averaged, seems to be obtained from powder neutron diffraction data; the same can be done using specific XRD and refinement techniques [188,193,194]. High

resolution electron microscopy (HREM), in conjunction with selected area electron diffraction (SAED) can be used to probe the local crystalline structure and detect defective or multi-phase areas [188,195,196].

It is clear, however, that one must question the adequacy of these physico-chemical procedures, usually carried out close to room temperature, or even lower, to supply usable data for those materials which are used at temperatures in excess of 300°C [187]. Besides, most of these procedures are extremely time consuming.

4.2.2. Chemical reactivity measurements

The best way to test the performance of any given zeolite or molecular sieve for a particular catalytic application will always be the catalytic reaction itself. However, the comparison and understanding of a catalyst's mode of action can be achieved by the choice of particular test reactions, designed to give as much information as possible and to establish rules that ultimately can be used for the preparation of new catalysts.

On the basis of the product distribution and using several zeolite samples, a number of criteria have been proposed for the characterisation of the zeolite intracrystalline space [169,187,197–215]. The use of catalytic test reactions for probing the pore structure of zeolites is a topic of considerable importance, as can be seen in Weitkamp's recent review of this subject [216].

Constraint Index (CI) – this test, presented by workers of the Mobil Res. Dev. Co. [169], depends on the selectivity for the competitive cracking of an equimolar mixture of n-hexane and 3-methylpentane, under specific conditions. The index is defined as:

constraint index

$$= \frac{\log (\text{fraction of n–hexane remaining})}{\log (\text{fraction of 3–methylpentane remaining})}$$

and approximates to the ratio of the first-order rate constants for the two cracking reactions. The reactions are acid-catalysed and the index is able to

distinguish between large and medium pore zeolites, without specifying any further the nature of the void volume [197]. This index has been critically examined, and was found to decrease with increasing reaction temperatures [198], to be dependent on the strength of the Brønsted acid sites and the presence of organic residues (coke) on the catalyst [199], and to be enhanced by the presence of minute quantities of a noble metal or pore mouth cracking [200] caused by crystal terminating hydroxyls. The numerical value of the CI increases as the pore width of the zeolite decreases. According to Frilette, the CI allows a classification of molecular sieve materials into three categories: large pore (12-MR: CI < 1), medium pore (10-MR: $1 \leq CI \leq 12$) and small pore (8-MR: CI > 12) [169].

m-Xylene conversion reaction – in this test, the ratio R of the rate constants for o-xylene to p-xylene formation from m-xylene, is used to inspect the zeolite's pore structure [187]:

$$R = \frac{k_1 \ (o\text{–xylene from } m\text{–xylene})}{k_2 \ (p\text{–xylene from } m\text{–xylene})}$$

This ratio depends on the transport properties of the zeolite pore structure (it is proportional to the ratio of the effective diffusion constants for the respective isomers) and it becomes a structural parameter, independent of the crystallite size, the distribution and strength of the active sites; furthermore, the values obtained for R are temperature-independent [187], becoming a reliable parameter for probing medium pore zeolites [188]. Nevertheless, it should be stressed that the deactivation rate will vary greatly (depending on the nature, pore size and acid strength of the zeolites), complicating the determination of initial rate constants [188].

Transformation of xylenes and 1,2,4-*trimethylbenzene* – in this test, the ratio of disproportionation to isomerisation rates, the ratio of the amount of hydrocarbon transformed into coke to the amount isomerised, the distribution of the primary products of isomerisation and the distribution of the disproportionation primary products of the transformation of xylenes and 1,2,4-trimethylben-

zene are the criteria to characterise the pore structure of intermediate pore size zeolite [201]. The observations over different zeolites were explained by these authors in terms of the three types of shape selectivity defined by Csicsery (see above) [128]. One of these reactions, the transformation of *m*-xylene, was claimed to be sufficient for this characterisation of the pore structure [201], and, in fact, constitutes an extension of the index *R*, presented above. The selectivity of its isomerisation is related to the pore size: the smaller the pore size, the more favoured should be the formation of the smaller isomer (*p*-xylene); the ratio between bimolecular reaction rates (disproportionation and coke formation) and the monomolecular reaction of isomerisation, is directly connected to the maximum space available to intermediates or transition states formation, leading to information about cages or channels intersection sizes.

Xylene transformation and ethylbenzene disproportionation – the acid-catalysed transformation of *m*-xylene can be used to classify zeolite void volumes in terms of 10- and 12-membered ring structures [188,197,202]. Since the trimethylbenzenes that are formed have distinctly different kinetic diameters [162] and the reaction is bimolecular, selectivity changes will be induced both by transition state shape selectivity and by changes in the diffusion pathways, which can be considered as a drawback. The formation of this bimolecular transition state can also be influenced by geometric constraints in the intracrystalline void volume, as well as by the density of sites [188]. It should be pointed out that with these reactions, the catalysts should be compared at constant temperature and conversion and also at equal coke content.

Also the disproportionation of ethylbenzene is a reliable test for void characterisation in zeolites [202,203], because of the small size of the feed. Although this reaction will suffer from the same limitations (distinction between diffusion and shape selectivity is difficult, transition state selectivity will be determined by site density as well as by void size, coking rates will differ with the zeo-

lite and comparison at equal degree of coking will be difficult) it can correctly classify zeolites in terms of large pores (12-MR) and medium pore (10-MR), provided 4 criteria are taken into account together [203]: (i) the presence of an induction period, which only occurs with large pore zeolites; (ii) the rate of deactivation, which is faster on large pore zeolites; (iii) the diethylbenzene/benzene product ratio, which is only near-stoichiometric with the large pore zeolites; (iv) the distribution of the diethylbenzene isomers.

Shape selectivity index – this method, designed for the evaluation of zeolite shape selective properties, uses the isomerisation of *m*-xylene as a test reaction [212]. The shape selectivity index (SSI) is defined as the limiting value of the product *para*-/*ortho*-xylene ratio, as the conversion of *m*-xylene approaches to zero, minus the corresponding ratio obtained under identical experimental conditions using a non-shape selective (nss) acid catalyst, e.g. amorphous silica–alumina:

$$SSI = \frac{k'_{mp}}{k'_{mo}} - \left[\frac{k'_{mp}}{k'_{mo}}\right]_{nss}$$

$$= \lim_{conv \to 0}\left[\frac{p}{o}\right] - \lim_{conv \to 0}\left[\frac{p}{o}\right]_{nss}$$

The application of the correction term $[p/o]_{nss}$, results in SSI$=0$ when no shape selectivity is apparent. The authors found values from 1.71 to 2.48 for SSI calculated for different steamed HZSM-5 zeolites.

Alkylation of meta-diisopropylbenzene with propylene – Recently [217], the weighted ratio of 1,3,5- to 1,2,4-triisopropylbenzene formed by monofunctional alkylation of *meta*-diisopropylbenzene with propylene, has been proposed to characterise the effective pore size of larger pore molecular sieve materials (12-MR or above): SAPO-5, Off, Mordenite, Beta, EMT, Fau, L, SAPO-37. This ratio, calculated at conversions near 25%, shows a strong correlation with pore/void size, i.e., the ratio increases with increasing size. This test seems to be specifically designed

for probing the pore of large and super-large pore molecular sieves [216].

Bifunctional conversion of naphthenes and alkylaromatics – the work reported on the bifunctional conversion of cyclodecane [204,205], ethylcyclohexane [206–208], mono-, bi- and tricyclonaphthenes [209] over zeolites loaded with no more than 1% by weight of noble metal, can be used to distinguish between ZSM-5 and ZSM-11 and consequently within the group of 10-MR zeolites. Although reaction networks are quite complex and each parameter selected to probe the void volume is, to some extent, temperature and conversion dependent, the data concerning cyclodecane [204,210] and butylcyclohexane [209] transformations have led to the derivation of two sensitive and quantitative criteria: (i) internal ring alkylation to *cis-* or *trans*-decalin is very much structure dependent [204,210] and the selectivity does not change in a wide range of temperatures [204]; (ii) high i-/n-butane ratios will be found if sufficient space is available [210]. A complete discussion of these two indexes can be found in [188].

Catalytic cracking of medium sized paraffins – when C_{6+} paraffins are cracked, it was shown that C_4/C_3 or C_4/C_2 ratios of the cracked products change with the zeolite [148]. Low C_4/C_3 ratios are typical of small pores or cages, accessible through 8-MR, and seem to be useful for the prediction of the presence of small cages or channels in unknown zeolite structures [148].

Bifunctional conversion of n-decane [174] – this reaction allows one to rank intracrystalline void volumes of zeolites in terms of connectivity of pores (12-MR, 10-MR) and in terms of the structure of this volume: 12-MR, pores, 12-MR windows with cages of different size and 8-MR windows limiting cages of different sizes [197]. Five criteria are used and interpolation of their values within those obtained for known zeolite structures, gives a fair prediction of the zeolite pore architecture [174,188,197]: (i) the refined constraint index ($CI°$), equal to the 2- to 5-methylnonanes product ratio at 5% isomerisation; (ii) the ethyloctane yield at 5% isomerisation; (iii)

the 3- to 4-ethyloctane ratio at different conversions; (iv) the yield of dibranched isomers at maximum isomerisation conversion; (v) the isopentane yield at 35% hydrocracking conversion.

Spaciousness index (SI) – the spaciousness index (SI) is defined as the yield ratio of isobutane and n-butane in hydrocracking of a C_{10}-naphthene over bifunctional zeolites or zeolite-like materials [211]. This ratio increases with increasing pore width, becoming a tool for characterising the shape selective properties of molecular sieve materials; palladium as hydrogenation component is recommended (around 0.27 wt.%). Under certain conditions, SI is independent of: (i) the reaction temperature; (ii) the nature and amount of noble metal; (iii) the SiO_2/Al_2O_3 ratio of the zeolite; (iv) the size of individual zeolite crystallites [211]. SI is especially sensitive in the transition region between the medium and the very large pore zeolites; in the other hand, in the range of pore widths at 10-membered ring zeolites (medium pore zeolites), SI seems to be less appropriate. For such materials, the refined constraint index [197] is probably more appropriate. It ranges from about 0 to 20 when the space available in the zeolite pores increases (ZSM-5 < Off ≪ Beta < Y).

1-Methyl-2-ethylbenzene (*1M2EB*) *test* – the transalkylation (to monoalkylbenzenes and trialkylbenzenes) and isomerisation reactions of 1M2EB are used as test reaction to characterise zeolite structures [213]. The authors claim that the 1M2EB test can reveal: (i) the minimum pore dimensions; (ii) the space available around the acid site; (iii) the acid strength; (iv) diffusion limitations; (v) optimum activation conditions; (vi) dehydrocyclization activity.

Heptadecane test – the hydrocracking of heptadecane on bifunctional zeolite catalysts of the FAU/EMT family, was found to be particularly suitable to locate the catalytic activity in the different cages presented by those zeolites [214,215]. The authors claim that this test is appropriate for characterising cubic and hexagonal faujasite phases and their intergrowths, as well as monitoring the generation of mesopores upon

dealumination of these zeolites. Hydrocracking of heptadecane in hypocages is detected by maxima at C_5 and C_{12} in the carbon number distribution of the cracked products [215]. The contribution of hypocage catalysis decreases in order EMC-2 > ZSM-2 > CSZ-1 > ZSM-3 > ZSM-20,   Y, SAPO-37, EMC-1. The most active sites are located in the mesopores, generated during dealumination; after steaming and acid leaching, hypocage catalysis seems to disappear, and ultrastable FAU and EMT phases catalyse heptadecane hydrocracking without molecular shape-selective constraints.

New super-large pore materials are emerging; the proposal of new test reactions is to be attained. The use of reactions involving other organic compounds, besides hydrocarbons, as probes for the effective pore width characterisation of microporous materials, in the near future, could also prove to be quite suitable [216].

4.3. Pore size modifications and external surface inactivation

Pore size modification is a very promising *engineering* process to increase the range of catalysts available. It can be used, alongside external surface modifications, to design a catalyst to be more selective, in the sense of shape selectivity, towards a certain reaction. This particular theme has been the subject of a recent review [218], so, it will only be addressed here in passing.

The techniques to alter the internal pore system of a zeolite can be divided into two main classes: (i) *transient* and (ii) *permanent* modifications. The former can be performed by pre-adsorption of polar molecules, such as water and amines [219], and coke deposition. The latter, that include the introduction of bulky compounds inside the porous structure of the zeolite, are commonly performed by ion exchange [6,220], silanation and disilanation, boranation, impregnation with organic and inorganic phosphorus compounds, and treatments with metal halides or organometallic compounds. Both the transient and the permanent modifications influ-

ence the accessibility and geometrical neighbourhood of the active sites, as well as the acidic properties of these sites.

Many of these methods also induce changes in the external surface of the zeolite particles and although the external surface of the zeolite crystals should account for only a very small percentage of the total surface area, the role of the catalytic sites on the external crystallite surface can not be neglected in some applications [221,222]. Some gains in selectivity have been obtained due to the inactivation of these surface sites, which do not possess shape selective properties. However, the distinction between surface inactivation and pore size reduction is unclear, since in many cases, both effects occur simultaneously.

4.3.1. Pore size modification

The internal implantation of polar groups by chemisorption of small inorganic molecules such as silane (SiH_4), disilanes (Si_2H_6) and boranes (B_2H_6), which are very reactive towards the hydroxyls groups of the zeolites, can originate changes in the pore dimensions and electrical field within the zeolite channels [223–229]. The effect of reducing the pore sizes using this technique has been analysed mainly for processes involving adsorption and separation of gaseous mixtures [230,231], but it shows also a great potential for shape-selective catalysis [228]. The extension and localisation of the modification can be controlled by the operating conditions, namely pressure of modified agent and temperature [227–229]. Concomitant modifications of the external surface can occur in for certain ranges of experimental conditions [229].

Modifications using halides have been reported by several authors. Treatments with $SiCl_4$ to stabilise and dealuminate Y zeolite are common practice; however, similar procedures applied to smaller pore zeolites, originate also surface or internal deposition. Hidalgo et al. [232] have examined the modification of mordenite with $SiCl_4$, $GeCl_4$, $TiCl_4$ and $SnCl_4$ and found metal chloride deposits either along the interior channel or only near the channel entrance depending on

the reactivity and molecular size of the halide, and on experimental conditions. Methanol conversion on these modified mordenites showed changes in selectivity and activity. Guisnet et al. found significant changes in the selectivity for aromatic production, during propane aromatization, in HZSM-5 samples with zinc deposited by reaction with zinc chloride [233].

4.3.2. External surface modification

Depending on the size of the zeolite pores and of the molecular size and reactivity of the modifying agent, it is possible to passivate the external surface, and simultaneously to control the pore-opening size, without affecting the internal pore structure and acidity. The methods that appear to be used most commonly consist in coating processes, performed mainly by chemical vapour deposition (CVD) of silicon compounds, impregnation with organic solutions of silicone polymers, and also by coking of the surface.

CVD of silicon alkoxides $Si(OCH_3)_4$, $Si(OC_2H_5)_4$ and $Ge(OCH_3)_4$, have been proposed by M. Niwa et al. [234–240] as a useful method for enhancing the shape-selectivity of zeolites. The alkoxides react with terminal silanol groups, leading, upon further decomposition reaction, to the coverage of zeolite crystal's surface. Deposition of silica or germanium oxide occurs on the external surface as a thin layer, which narrows the pore openings of zeolites and simultaneously deactivates acid sites on the external surface, without changing the internal properties of the zeolite, as confirmed by ammonia TPD [234,235]. This method has been applied to H-mordenite [234–237] and HZSM-5 [238,239] and their shape selectivities have been improved in hydrocracking of paraffins, cracking of octane isomers, methanol conversion, alkylation of toluene with methanol and toluene disproportionation. Recently Hibino et al. [240] found that the silicon concentration required for the inactivation of the external surface, on mordenites and ZSM-5, does not depend on the Si/Al ratio. This technique has attracted much attention from various researchers that have been using deposition of

$Si(OC_2H_5)_4$ to improve the catalytic stability of zeolite for cumene disproportionation [241], or to enhance shape selectivity of ZSM-48 in xylene isomerization [242].

Other methods that have been reported in literature to passivate external surface include the work of Kaeding et al. [243] using carborane–silicone polymer to deactivate the external surface of ZSM-5, impregnation of ZSM-5 with dimethylsilicone polymer [244], to enhance *para*-selectivity during toluene disproportionation, albeit with a decrease of catalytic activity, and, recently, the replacement of acidic protons on the external surface by lithium ions from a lithium complex with a crown ether (dicyclo-18-crown-6) [245]. The deposition of bulky organometallic complexes such as MBu_4, MPh_4, (M = Sn, Ge), $ZrNp_4$ and $MgNp_2$, on the external surface of mordenite, followed by a calcination procedure, produces, in certain cases, an improvement of the catalytic behaviour of mordenite-based catalysts during the isomerisation of a C_8 aromatic cut [246].

If the operating conditions are carefully selected, it is possible to use conventional internal modifiers to perform external modifications selectively. This is the case, for instance, of the treatments with $SiCl_4$ or $SiF_6(NH_4)_2$, which are commonly used to dealuminate internal structures of large pore zeolites, but due to its high reactivity is possible to control the deposition so that it occurs mainly on the surface of the crystals. The treatment of ZSM-5 with $SiCl_4$ studied by Namba [247] and Anderson et al. [248] produced materials that were surface enriched in silicon. Also, ZSM-5 treated with $SiF_6(NH_4)_2$, have silicon enriched surfaces showing a decrease of disproportionation reaction during *m*-xylene isomerization [249], as shown in Fig. 9. The effects of surface passivation have also been observed in the increase of *o*-hydroxyacetophenone, in the phenol acylation reaction over HZSM-5 [250].

External modification using disilane, also an internal modifying agent, can occur when high reaction temperatures are used. Increasing the chemisorption temperature, increases the reactiv-
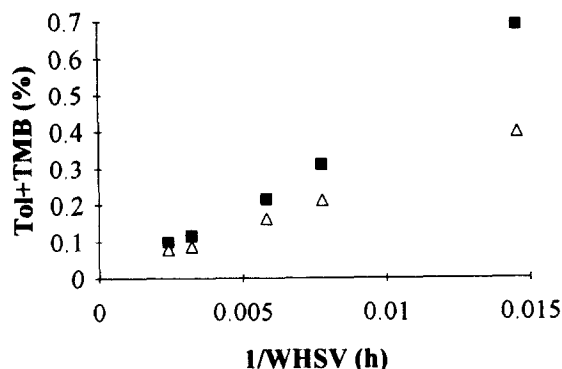
Fig. 9. Change of the disproportionation activity as a function of WHSV for an MFI sample with a Si/Al ratio of 28, before (■) and after (△) silica deposition (from ref. [249]).

ity between disilane molecules and the structural OH groups. Under these conditions, the entering disilane molecules immediately react with OH groups on the external surface and at the pore entrances. These chemisorbed molecules prevent the other disilane molecules from diffusing into the internal pore system [228,229]. Therefore, the modification at higher temperature produces a substrate with smaller pore size and without much loss in the internal volume, which can be advantageous for some catalytic applications.

For small pore size zeolites, such as HRHO zeolite, it was also possible to deactivate external acidic sites with trimethylphosphite without affecting neither the zeolite pore size nor the internal acidic sites, improving the selectivity for the synthesis of methylamines from methanol and ammonia [251].

Finally, the coking of zeolites can also be considered as a technique for the inactivation of the external surface of zeolites. The coke formation in zeolite catalysts is essentially determined by their structural properties, and for smaller pore sizes such as ZSM-5 it takes place mainly on the external surface [140,252]. During the conversion reaction of methanol to hydrocarbons on ZSM-5, it is observed that the carbonaceous residues are primarily formed on the outer surface of the crystallites, resulting only in a slight modification of its molecular shape-selectivity properties and producing a high resistance to aging, as

opposed to the case of offretite or mordenite, where the channels are large enough to accommodate carbonaceous residues, which lead to a drastic loss of catalytic activity and very rapid aging [253]. For toluene disproportionation or alkylation with methanol and ethylene on ZSM-5 [243,254] the selectivity to *p*-xylene is significantly increased by coke deposits which deactivate the acid sites of the external surface, thus avoiding the secondary isomerization of the product.

5. Conclusions

From all the work presented here, we conclude that the development in the field of zeolitic catalysis, not only in the traditional areas in the petroleum and petrochemical industries, has opened a whole new range of possibilities for the use of these materials.

The range of catalysts available, as well as the gamut of post-synthesis treatments to modify the catalytic properties of these materials, is rapidly increasing. The amount of publications cited in this review (and many more have been, unfortunately, left out) is a clear indication of the vitality of this field. It is our belief that the possibility to fine-tune the catalytic properties of zeolitic materials will continue to increase, either by synthetic or post-synthetic procedures.

There are two main ways of development that are now open, and where we would expect to see a significant improvement: (i) synthesis of larger pore zeolites; (ii) application of the new zeolitic materials to new processes.

The appearance of zeolites possessing pore openings with more than 12 T-atoms, previously predicted by theory [255], like VPI-5, AlPO-54 and MCM-9 [256], has already opened the way to the application of zeolites to the processing of larger molecules, eventually leading to new perspectives in shape-selective catalysis.

We hope that the enormous advance that this field has known in the last few years will also result in the propagation of new applications that

will benefit from the enhanced activity and selectivity that can be achieved by the use of these materials and that will contribute to a cleaner and more efficient chemical industry.

References

[1] I.E. Maxwell and W.J. Stork, Stud. Surf. Sci. Catal., 58 (1991) 571.

[2] A. Corma, in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer Academic Publishers, Dordrecht, 1992, p. 373.

[3] G. Perot and M. Guisnet, J. Mol. Catal., 61 (1990) 173.

[4] W.F. Hölderich and H. van Bekkum, Stud. Surf. Sci. Catal., 58 (1991) 631.

[5] Y. Ben Taarit, in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer, Dordrecht, 1992, p.291.

[6] D.W. Breck, Zeolite Molecular Sieves, J. Wiley and Sons, New York, 1974.

[7] P.A. Jacobs, Carboniogenic Activity of Zeolites, Elsevier, Amsterdam, 1977.

[8] P.A. Jacobs and J.A. Martens, Stud. Surf. Sci. Cat., 58 (1991) 445.

[9] D. Barthomeuf, Mater. Chem. Phys., 17 (1987) 49.

[10] B. Coq, J. Pardillos and F. Figueras, Appl. Catal., 62 (1990) 281.

[11] W.J. Mortier, J. Catal., 55 (1978) 138.

[12] J.M. Lopes, F. Lemos, F. Ramôa Ribeiro, E. Derouane, P. Magnoux and M. Guisnet, Appl. Catal. A, 114 (1994) 161.

[13] J.M. Lopes, F. Lemos, F. Ramôa Ribeiro and E. Derouane, Appl. Catal., A, 119 (1994) 139.

[14] V.R. Choudhary and D.B. Akolekar, J. Catal., 119 (1989) 525.

[15] V.R. Choudhary and D.B. Akolekar, J. Catal., 125 (1990) 143.

[16] A. Corma, P.J. Miguel, A.V. Orchillés and G. Koermer, J. Catal., 145 (1994) 181.

[17] D. Barthomeuf, in F. Ramôa Ribeiro et al. (Eds.), Zeolites: Science and Technology, NATO ASI Series E 80, Martinus Nijhoff, The Hague, 1984, p.317.

[18] G.J. Kramer and R.A. van Santen, J. Am. Chem. Soc., 115 (1993) 2887.

[19] I.N. Senchenya, V.B.Kazansky and S. Beran, J. Phys. Chem., 90 (1986) 4857.

[20] S. Beran, J. Phys. Chem., 94 (1990) 335.

[21] R.A. van Santen, D.P. de Bruyn, C.J.J. den Ouden and B. Smit, Stud. Surf. Sci. Catal., 58 (1991) 317.

[22] J. Dwyer, in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer, Dordrecht, 1992, p.321.

[23] A. Corma, F.V. Melo and D.J. Rawlence, Zeolites, 10 (1990) 690.

[24] L.A. Pine, P.J. Maher e W.A. Wachter, J. Catal., 85 (1984) 466.

[25] A. Corma, F. Llopis and J.B. Monton, J. Catal., 140 (1993) 384.

[26] M.F. Ribeiro, F. Lemos, F. Ramôa Ribeiro, Ch. Travers, F. Raatz and Ch. Marcilly, in H.J. Lovink and G.J. Antos (Eds.), Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons by Heterogeneous Catalysis, American Chemical Society, Washington, DC, 36(4) (1991).

[27] A. Macedo, F. Raatz, R. Boulet, A. Janin and J.C. Lavalley, Stud. Surf. Sci. Catal., 37 (1988) 375.

[28] D. Chen, S. Sharma, N. Cardona-Matínez, J.A. Dumesic, V.A. Bell, G.D. Hodge and R.J. Madon, J. Catal., 136 (1992) 392.

[29] N.P. Rhodes and R. Rudham, J. Chem. Soc., Faraday Trans., 89(14) (1993) 2551.

[30] Q.L. Wang, G. Gianneto and M. Guisnet, J. Catal., 130 (1991) 471.

[31] Z. Liu and B. Dadyburjor, J. Catal., 134 (1992) 583.

[32] F. Lemos, PhD Thesis, Instituto Superior Técnico, 1989, Lisboa.

[33] J.M. Lopes, PhD Thesis, Instituto Superior Técnico, 1993, Lisboa.

[34] Y.S. Chen, M. Guisnet, M. Kern, J.L. Lemberton, New J. Chem., 11(8–9) (1987) 623.

[35] R. Kumar, W.-C. Cheng, K. Rajagopalan, A.W. Peters and P. Basu, J. Catal., 143 (1993) 594.

[36] J. Scherzer, Catal. Rev.-Sci. Eng., 31(3) (1989) 215.

[37] F. Lemos, F. Ramôa Ribeiro, G. Gianneto, M. Kern and M. Guisnet, Appl. Catal., 29 (1987) 43.

[38] A. Corma, V. Fornés, J.B. Monton and A.V. Orchillés, Ind. Eng. Chem. Prod. Res. Dev., 25(2) (1986) 231.

[39] F. Lemos, F. Ramôa Ribeiro, G. Gianneto, M. Kern and M. Guisnet, Appl. Catal., 39 (1988) 227.

[40] F. Lemos, J.M. Lopes and F. Ramôa Ribeiro, J. Mol. Catal., 53 (1989) 265.

[41] F. Lemos, J.M. Lopes, F. Ramôa Ribeiro and M. Guisnet, React. Kinet. Catal. Lett., 41(2) (1990) 351.

[42] R. Carvajal, P.-J. Chu and J.H. Lunsford, J. Catal., 44(5) (1990) 519.

[43] F. Lemos, J.M. Lopes, F. Ramôa Ribeiro and E.G. Derouane, Appl. Catal., 49 (1989) 175.

[44] E.F.T. Lee and L.V. Rees, Zeolites, 7 (1987) 143.

[45] F. Maugé, P. Gallezot, J.-C. Courcelle, P. Engelhard and J. Grosmangin, Zeolites, 6 (1986) 261.

[46] S.E. Tung and E.J. McIninch, J. Catal., 10 (1968) 166.

[47] W.J. Wojciechowski and A. Corma, Catalytic Cracking, Marcel Dekker, New York, 1986.

[48] B.C. Gates, J.R. Katzer and G.C.A. Schmit, Chemistry of Catalytic Processes, McGraw-Hill, New York, 1979.

[49] W.O. Haag and R.M. Dessau, Proc. 8th Int. Congr. Catal., Berlim, Vol. 2 (1984) p.305.

[50] A. Corma, J. Planelles and F. Tomás, J. Catal., 94 (1985) 445.

[51] C. Mirodatos and D. Barthomeuf, J. Catal., 114 (1988) 121.

[52] A.F.H. Wielers, M. Vaarkamp and M.F.M. Post, J. Catal., 1237 (1991) 51.

[53] A. Corma, G. Sastre, R. Viruela and Z. Zicovich-Wilson, J. Catal., 136 (1992) 521.

[54] L.A. Pine, P.J. Maher and W.A. Wachter, J. Catal., 85 (1984) 466.

[55] E. van Broekhoven and H. Wijngaards, in H.J. Lovink (Ed.), Akzo Catalysts Symposium '88, Akzo Chemicals, Amersfoort, 1988, section F-8.

[56] K. Rajagopalan and A.W. Peters, J. Catal., 106 (1987) 410.

[57] A. Corma, M. Faraldos and A. Mifsud, Appl. Catal., 47 (1989) 125.

[58] K.A. Van Genechten and W.J. Mortier, Zeolites, 8 (1988) 273.

[59] M.L. Poutsma and S.R. Schaffer, J. Phys. Chem., 77 (1973) 158.

[60] J.A. Rabo and M.L. Poutsma, Adv. Chem., 102 (1971) 284.

[61] P.H. Espeel, M. Tielen and P.A. Jacobs, J. Chem. Soc., Chem. Commun., (1991) 669.

[62] I.E. Maxwell, Adv. Catal., 31 (1982) 1.

[63] C. Yang and Z. Meng, J. Catal., 142 (1993) 37.

[64] M. Guisnet and N.S. Gnep, in Zeolites: Science and Technology, F. Ramôa Ribeiro et al. (Eds.); NATO ASI Series E 80, Martinus Nijhoff, The Hague, 1984, p.571.

[65] W.F. Hoelderich, Stud. Surf. Sci. Catal., 41 (1988) 83.

[66] D. Kalló and G. Onyestyák, J. Mol. Catal., 62 (1990) 307.

[67] R.A. Schoonheydt, Catal. Rev.-Sci. Eng., 35(1) (1993) 129.

[68] M.W. Simon, A.M. Efstathiou, C.O Bennett and S.L. Suib, J. Catal., 138 (1992) 323.

[69] J.O. Petunchi, G.A. Sill and W.K. Hall, J. Catal., 141 (1993) 323.

[70] D. Barthomeuf and A. Mallmann, Stud. Surf. Sci. Catal., 37 (1988) 365.

[71] P.E. Hathaway and M.E. Davis, J. Catal., 116 (1989) 279.

[72] A. Corma, V. Fornés, R.M. Martín-Aranda, H. García and J. Primo, Appl. Catal., 59 (1990) 237.

[73] K. Tanabe, Stud. Surf. Sci. Catal., 20 (1985) 1.

[74] L.R.M. Martens, P.J. Grobet and P.A. Jacobs, Nature, 315 (1985) 568.

[75] P.E. Hathaway and M.E. Davis, J. Catal., 116 (1989) 263.

[76] R.M. Martens, P.J. Grobet, W.J.M. Vermeiren and P.A. Jacobs, Stud. Surf. Sci. Catal., 28, (1986) 67.

[77] T. Yashima, H. Suzuki and N. Hara, J. Catal., 33 (1974) 486.

[78] D. Barthomeuf, G. Coudurier and J.C. Vedrine, Mater. Chem. Phys., 18(5–6) (1988) 553.

[79] Y. Okamoto, M. Ogawa, A. Maezawa and T. Imanaka, J. Catal., 112 (1988) 427.

[80] D. Barthomeuf, J. Phys. Chem., 88 (1984) 42.

[81] E.G. Derouane, J.-M. Andre and A.A. Lucas, J. Catal., 110 (1988) 58.

[82] E.M. Flanigen, Stud. Surf. Sci. Catal., 58 (1991) 13.

[83] J. Weitkamp, S. Ernst, B. Günzel and W.-D. Deckwer, Zeolites, 11 (1991) 314.

[84] F. Fajula, R. Ibarra, F. Figueras and C. Gueguen, J. Catal., 89 (1984) 60.

[85] M. Tielen, M. Geelen and P.A. Jacobs, Acta Phys. Chem., 31 (1985) 1.

[86] W.E. Holderich, Stud. Surf. Sci. Catal., 49(A) (1989) 69.

[87] D.H. Dompas, W.J. Mortier, O.C.H. Kenter, M.J.G. Janssen and J.P Verduijn, J. Catal., 129 (1991) 19.

[88] N. Gnep, A.M. Seco, F. Ramôa Ribeiro and M. Guisnet, Appl. Catal., 43 (1988) 155.

[89] M.S. Scurrell, Appl. Catal., 32 (1987) 1422.

[90] A.J. Chandwadkar, R.A. Abdulla, S.G. Hegde and J.B. Nagy, Zeolites, 13 (1993) 470.

[91] M.A. Camblor, J. Pérez-Pariente and V. Fornés, Zeolites, 12 (1992) 280.

[92] Z.G. Zulfugarov, A.S. Suleimanov and Ch.R. Samedov, Stud. Surf. Sci. Catal., 18 (1984) 167.

[93] A. Corma, R.M. Martín-Aranda and F. Sánchez, J. Catal., 126 (1990) 192.

[94] D. Barthomeuf, in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer, Dordrecht, 1992, p. 193.

[95] J.A. Rabo in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer, Dordrecht, 1992, p. 531.

[96] W.F. Hoelderich in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer, Dordrecht, 1992, p. 579.

[97] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajak, T.R. Cannan and E.M. Flanigen, J. Am. Chem. Soc., 106 (1984) 6092.

[98] R.J. Pellet, G.N. and J.A. Rabo, Stud. Surf. Sci. Catal., 28 (1986) 843.

[99] E.G. Derouane, J.B. Nagy, C. Fernandez, Z. Gabelica, E. Laurent and P. Maljean, Appl. Catal., 40 (1988) L1.

[100] M. Mertens, J.A. Martens, P.J. Grobet and P.A. Jacobs, in D. Barthomeuf et al. (Eds.), Guidelines for Mastering the Properties of Molecular Sieves, NATO ASI Series B 221, Plenum Press, New York, 1990, p. 1.

[101] E.M. Flanigen, R.L. Patton and S.T. Wilson, Stud. Surf. Sci. Catal., 37 (1988) 13.

[102] L.S. Saldarriaga, C. Saldarriaga and M.E. Davis, J. Am. Chem. Soc., 106 (1987) 2689.

[103] D. Hasha, L.S. Saldarriaga, C. Saldarriaga, P.E. Hathaway, D.F. Cox and M.E. Davis, J. Am. Chem. Soc., 110 (1988) 2127.

[104] L.B. Young, S.A. Butler and W.W. Kaeding, J. Catal., 76 (1982) 418.

[105] J. Numan, J. Cronin and Cunningham, J. Catal., 87 (1984) 77.

[106] J. Liang, H. Li, S. Zhao, W. Guo, R. Wang and M. Ying, Appl. Catal., 64 (1990) 31.

[107] A.J. Marchi and G.F. Froment, Appl. Catal., 71 (1991) 139.

[108] R.J. Pellet, P.K. Coughlin, E.S. Shamshoum and J.A. Rabo, ACS Symp. Ser., 368 (1988) 512.

[109] S.J. Choung and J.B. Butt, Appl. Catal., 64 (1990) 173.

[110] S. Hocevar and J. Levec, J. Catal., 135 (1992) 518.

[111] J.A. Martens, C.Janssens, P.J. Grobet, H.K. Beyer and P.A. Jacobs, Stud. Surf. Sci. Catal., 49(A) (1989) 215.

[112] T. Inui, H. Matsuda, H. Okaniwa and A. Miyamoto, Appl. Catal., 58 (1990) 155.

[113] S.G. Edge, P. Ratnasamy, L.M. Kustov and V.B. Kazansky, Zeolites, 8 (1988) 137.

[114] J.M. Lopes, F. Lemos, F. Ramôa Ribeiro and E.G. Derouane, Stud. Surf. Sci. Catal., 69 (1991) 365.

[115] M. Briend, M.J. Peltre, A. Lamy, P.P. Man and D. Barthomeuf, J. Catal., 138 (1992) 90.

[116] B.L. Su and D. Barthomeuf, Zeolites, 13 (1993) 626.

[117] B.L. Su and D. Barthomeuf, J. Catal., 139 (1993) 81.

[118] J.A. Martens, P.J. Grobet and P.A. Jacobs, J. Catal., 126 (1990) 299.

[119] L. Maistriau, N. Dumont, J.B. Nagy, Z. Gabelica and E.G. Derouane, Zeolites, 10 (1990) 243.

[120] B.Z. Wan and K. Huang, Appl. Catal., 73 (1991) 113.

[121] C. Montes, M.E. Davis, B. Murray and M. Narayana, J. Phys. Chem., 94 (1990) 6425.

[122] D.J. Parrillo, C. Pereira, G.T. Kokotailo and R.J. Gorte, J. Catal., 138 (1992) 377.

[123] S. Hocevar, J. Batista and V. Kaucic, J. Catal., 139 (1993) 351.

[124] M.E. Davis, Acc. Chem. Res., 28 (1993) 111.

[125] P.B. Weisz and V.J. Frilette, J. Phys. Chem, 64 (1960) 382.

[126] P.B. Weisz, V.J. Frilette, R.W. Maatman and E.B. Mower, J. Catal., 1 (1962) 307.

[127] N.Y. Chen, Z. Mazink, A.B. Schwartz and P.B. Weisz, Oil Gas J., 66 (1968) 154.

[128] S. M. Csicsery, in J.A. Rabo (Ed.), Zeolite Chemistry and Catalysis, ACS Monograph 171, American Chemical Society, Washington, DC, 1976, p. 680.

[129] R.J. Argauer and G.R. Landolt, US Pat. 3,702,866 (14 November 1972).

[130] N.Y. Chen, W.W. Kaeding and F.G. Dwyer, J. Am. Chem. Soc., 101 (1979) 6783.

[131] L.D. Rollmann and D.E. Walsh, in J.L. Figueiredo (Ed.), Progress in Catalyst Deactivation, NATO ASI Series, Martinus Nijhoff Publishers, The Hague, 1982, p. 81.

[132] E.G. Derouane, Stud. Surf. Sci. Cat., 20 (1985) 221.

[133] M. Guisnet and P. Magnoux, in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer Academic Publishers, Dordrecht, 1992, p. 473.

[134] N.Y. Chen, W.E. Garwood and F.G. Dwyer, Shape Selective Catalysis in Industrial Applications, Marcel Dekker, New York, 1989.

[135] H. van Bekkum and H.W. Kouwenhoven, Stud. Surf. Sci. Cat., 41 (1988) 45.

[136] W.F. Höelderich, M. Hesse and F. Naumann, Angew. Chem., Int. Ed. Engl., 27 (1988) 226.

[137] W.F. Höelderich, in D. Barthomeuf et al. (Eds.), Guidelines for Mastering the Properties of Molecular Sieves, NATO ASI Series B 221, Plenum Press, New York, 1990, p.319.

[138] S.M. Csicsery, Zeolites, 4 (1984) 202.

[139] S.M. Csicsery, Pure Appl. Chem., 58 (1986) 841.

[140] E.G. Derouane, Stud. Surf. Sci. Cat., 5 (1985) 5.

[141] E.G. Derouane, in F. Ramôa Ribeiro et al. (Eds.), Zeolites: Science and Technology, NATO ASI Series E 80, Martinus Nijhoff Publishers, The Hague, 1984, p. 347.

[142] P.B. Weisz, Pure Appl. Chem., 52 (1980) 2091.

[143] S.L. Meisel, J.P. McCullough, C.H. Lechthaler and P.B. Weisz, Leo Friend Symposium, American Chemical Society, Chicago, 1977.

[144] J.A. Rabo, R. Bezman and M.L. Poutsma, Acta Phys. Chem., 24 (1987) 39.

[145] E.G. Derouane and Z. Gabelica, J. Catal., 65 (1980) 486.

[146] E.G. Derouane, P. Dejaifve and Z. Gabelica, J. Chem. Soc., Faraday Discuss., 72 (1982) 331.

[147] C. Mirodatos and D. Barthomeuf, J. Catal., 57 (1979) 136.

[148] C. Mirodatos and D. Barthomeuf, J. Catal., 93 (1985) 246.

[149] P.B. Weisz, Chem. Technol., 3 (1973) 498.

[150] N.Y. Chen and P.B. Weisz, Chem. Eng. Progr. Symp. Ser., 73 (1967) 86.

[151] D.H. Olson and W.O. Haag, Am. Chem. Soc. Symp. Ser., 248 (1984) 275.

[152] J.N. Miale, N.Y. Chen and P.B. Weisz, J. Catal., 6 (1966) 278.

[153] C.D. Chang, Catal. Rev.-Sci. Eng., 25 (1983) 1.

[154] G. Giannetto, F. Alvarez, F. Ramôa Ribeiro, G. Pérot and M. Guisnet, in D. Barthomeuf et al. (Eds.), Guidelines for Mastering the Properties of Molecular Sieves, NATO ASI Series B 221, Plenum Press, New York, 1990, p. 355.

[155] P.A. Jacobs, J.A. Martens, J. Weitkamp and H.K. Beyer, J. Chem. Soc., Faraday Discuss., 72 (1982) 353.

[156] C.F. Ren, G. Coudurier and C. Naccache, in Y. Murakami et al. (Eds.), New Developments in Zeolite Science and Technology, Stud. Surf. Sci. Catal., vol. 28, Elsevier, Amsterdam, 1986, p. 733.

[157] A. Corma, M.J. Climent, H. Garcia and J. Primo, Appl. Catal., 49 (1989) 109.

[158] R. Kumar and P. Ratnasamy, J. Catal., 116 (1989) 440.

[159] R. Kumar, G.N. Rao and P. Ratnasamy, Stud. Surf. Sci. Catal., 49(B) (1989) 1141.

[160] J. Bandiera and Y. Ben Taarit, Appl. Catal., 76 (1991) 199.

[161] S.J. Rane and D.K. Chakrabarty, Appl. Catal. A, 93 (1993) 191.

[162] S.M. Csicsery, J. Catal., 23 (1971) 124.

[163] W.O. Haag and F.G. Dwyer, Aromatics Processing with Intermediate Pore Size Zeolite Catalysts, Am. Inst. Chem. Eng. Annu. Meet., 1979.

[164] N.S. Gnep, J. Tejada and M. Guisnet, Bull. Soc. Chim. Fr., I-5 (1982).

[165] L.B. Young, US Pat. 3,962,364 (1976).

[166] J.A. Martens, M. Wydoodt, P. Espeel and P.A. Jacobs, Stud. Surf. Sci. Catal., 78 (1993) 527.

[167] C.D. Chang, W.H. Lang and W.K. Bell, in W.R. Moser (Eds.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1981, p. 73.

[168] W.O. Haag, R.M. Lago and P.B. Weisz, J. Chem. Soc., Faraday Discuss., 72 (1982) 317.

[169] V.J. Frilette, W.O. Haag and R.M. Lago, J. Catal., 67 (1981) 218.

[170] W.O. Haag and R.M. Dessau, Proc. 8th Int. Congr. Cat., Dechema, vol.2, 1984, p. 305.

[171] F. Chevalier, M. Guisnet and R. Maurel, in G.C. Bond et al. (Eds.), Proc. 6th Int. Congr. Cat., The Chemical Society, London, 1977, p. 478.

[172] D.M. Brower and J.M. Oelderik, Recl. Trav. Chim. Pays-Bas, 87 (1968) 721.

[173] J. Weitkamp, Ind. Eng. Chem., Prod. Res. Dev., 21 (1982) 550.

[174] J.A. Martens, M. Tialen, P.A. Jacobs and J. Weitkamp, Zeolites, 4 (1984) 98.

[175] J.A. Martens and P.A. Jacobs, in J.B. Moffat (Ed.), Theoretical Aspects of Heterogeneous Catalysis, Van Nostrand Reinhold, New York, 1990, p. 52.

[176] F. Alvarez, PhD Thesis, Université de Poitiers, France, 1987.

[177] M. Guisnet, F. Alvarez, G. Giannetto and G. Pérot, Catal. Today, 1 (1987) 415.

[178] J. Weitkamp, P.A. Jacobs and J.A. Martens, Appl. Catal., 8 (1983) 123.

[179] P. Gallezot, A. Giroir-Fendler and D. Richard, Catal. Lett., 5 (1990) 169.

[180] Kh. Minachev, O.M. Nefedov, V.V. Kharlamov, S.Y. Panov and S.F. Politanskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1490.

[181] B. Notari, Stud. Surf. Sci. Catal., 37 (1988) 413.

[182] A. Esposito, M. Taramasso, C. Neri and F. Buonomo, US Pat. 4,396,783 (1983).

[183] P.R. Prasad Rao and A.V. Ramaswamy, Appl. Catal. A, 93 (1993) 123.

[184] C. Neri, A. Esposito, B. Anfossi and F. Buonomo, US Pat. 2,116,974 (1985).

[185] D.R.C. Huybrechts, L. De Bruycker and P.A. Jacobs, Nature, 345 (1990) 240.

[186] T. Tatsumi, M. Nakamura, S. Negishi and H. Tominaga, J. Chem. Soc., Chem. Commun., (1990) 476.

[187] J. Dewing, J. Mol. Catal., 27 (1984) 25.

[188] P.A. Jacobs and J.A. Martens, Stud. Surf. Sci. Catal., 28 (1986) 23.

[189] D.H. Olson, G.T. Kokotailo, S.L. Lawton and W.M. Meier, J. Phys. Chem., 85 (1981) 2238.

[190] G.T. Kokotailo, J.L. Schlenker, F.G. Dwyer and E.W. Valyocsik, Zeolites, 5 (1985) 349.

[191] A.C. Rohrman, R.B. Lapierre, J.L. Schlenker, J.D. Wood, E.M. Valyocsik, M.K. Rubin, J.B. Higgins and W.J. Rohrbaugh, Zeolites, 5 (1985) 352.

[192] J.L. Schlenker, W.J. Rohrbaugh, P. Chu, E.M. Valyocsik and G.T. Kokotailo, Zeolites, 5 (1985) 355.

[193] L.R. Gellens, W.J. Mortier, R.A. Schoonheydt and J.B. Uytterhoeven, J. Phys. Chem., 85 (1981) 2783.

[194] J.J. Pluth and J.V. Smith, J. Am. Chem. Soc., 102 (1980) 4704.

[195] G.R. Millward, J.M. Thomas, S. Ramdas and M.T. Barlow, in D. Olson and A. Bisio (Eds.), Proc. 6th Int. Zeolite Conf. Reno, Butterworths, Guildford, 1984, p. 793.

[196] J.M. Newsam, in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer Academic Publishers, Dordrecht, 1992, p. 167.

[197] J.A. Martens and P.A. Jacobs, Zeolites, 6 (1986) 334.

[198] W.O. Haag and R.M. Dessau, Proc. 8th Int. Congr. Catal. Berlin, Vol. II, Verlag Chemie, Weinheim, 1984, p. 305.

[199] F.R. Ribeiro, F. Lemos, G. Perot and M. Guisnet, in R. Setton (Ed.), Chemical Reactions in Organic and Inorganic Constrained Systems, NATO ASI Series C 165, 1986, p. 145.

[200] M. Guisnet, G. Giannetto, P. Hilaireau and G. Perot, J. Chem. Soc., Chem. Commun. (1983) 1411.

[201] N.G. Gnep, J. Tejada and M. Guisnet, Bull. Soc. Chim. Fr., (1982) - 5.

[202] H.G. Karge, J. Ladebeck, Z. Sarbak and K. Hatada, Zeolites, 2 (1982) 94.

[203] J. Weitkamp, S. Ernst, P.A. Jacobs and H.G. Karge, Petrochem. Brennst.-Chem., 39(1) (1986) 13.

[204] P.A. Jacobs and M. Tielen, Proc. 8th Int. Congr. Catal. Berlin, Vol. IV, Verlag Chemie, Weinheim, 1984, p. 357.

[205] P.A. Jacobs, M. Tielen, J.A. Martens and H.K. Beyer, J. Mol. Catal., 27 (1984) 11.

[206] R.C. Sosa, M. Nitta, H.K. Beyer and P.A. Jacobs, in D. Olson and A. Bisio (Eds.), Proc. 6th Int. Zeolite Conf. Reno, Butterworths (Pub.), Guildford, 1984, p. 508.

[207] J. Weitkamp, P.A. Jacobs and S. Ernst, Stud. Surf. Sci. Catal., 18 (1984) 279.

[208] R.C. Sosa, H.K. Beyer and P.A. Jacobs, Proc. 9th Symp. Ibero-Am. Catal., Vol II, 1984, p. 175.

[209] S. Ernst, J. Weitkamp, Proc. Int. Symp. Zeolite Catal. – ZEOCAT, Siófok, 1985, p. 457.

[210] P.A. Jacobs, M. Tielen and R.C. Sosa, Stud. Surf. Sci. Catal., 18 (1984) 175.

[211] J. Weitkamp, S. Ernst and C.Y. Chen, Stud. Surf. Sci. Catal., 49(B) (1989) 1115.

[212] F. Joensen, N. Blom, N.J. Tapp, E.G. Derouane and C. Fernandez, Stud. Surf. Sci. Catal., 49(A) (1989) 1131.

[213] S.M. Csicsery, J. Catal., 108 (1987) 433.

[214] J.A. Martens, M. Tielen and P.A. Jacobs, Stud. Surf. Sci. Catal., 46 (1989) 49.

[215] J.A. Martens, G.M. Vanbutsele and P.A. Jacobs, in R. von Ballmoos, J.B. Higgins and M.M.J. Treacy (Eds.), Proc. 9th Int. Zeolite Conf. Montreal, Vol. II, Butterworth, Stoneham, 1993, p. 355.

[216] J. Weitkamp and S. Ernst, Catal. Today, 9 (1994) 107.

[217] M.-H. Kim, C.-Y. Chen and M.E. Davis in M.E. Davis and S.L.Suib (Eds.), Selectivity in Catalysis, ACS Symp. Ser., 517 (1993) 222.

[218] F. Ramôa Ribeiro, Catal. Lett., 22 (1993) 107.

[219] R.M. Barrer and L.V. Rees, Trans. Faraday Soc., 50 (1954) 852.

[220] D.W. Breck, D.G. Eversole, R.M. Milton, T.B. Reed and T.L. Thomas, J. Am. Chem. Soc., 78 (1956) 5963.

[221] D. Fraenkel, Ind. Eng. Chem. Res., 29 (1990) 1814.

[222] G. Paparatto, G. de Alberti, G. Leofanti and M. Padovan, Stud. Surf. Sci. Catal., 44 (1989) 255.

[223] E.F. Vansant (Ed.), Pore Size Engineering in Zeolites, John Wiley and Sons, New York, 1990.

[224] R.M. Barrer, R.G. Jenkins and G. Peeters, in J.R. Katzer (Ed.), Molecular Sieves II, ACS Symp. Ser. 40 (1977) 258.

[225] A. Thijs, G. Peeters, E.F. Vansant, I. Verhaert and P. De Bievre, J. Chem. Soc., Faraday Trans. I, 79 (1983) 2821.

[226] E.F. Vansant, Stud. Surf. Sci. Catal., 37 (1988) 143.

[227] A. Thijs, S. Peeters, E.F. Vansant, G. Peeters and I. Verhaert, J. Chem. Soc., Faraday Trans. I, 82 (1986) 963.

[228] Y. Yan, J. Verbiest, P. De Hulsters, E.F. Vansant, J. Chem. Soc., Faraday Trans. I, 85 (1989) 3087, 3095.

[229] Y. Yan, J. Verbiest, E.F. Vansant, J. Philippaerts and P. De Hulsters, Zeolites, 10 (1990) 137.

[230] A.A. Jentys, G. Rumplmayr and J.A. Lercher, Appl. Catal., 53 (1989) 299.

[231] G. Rumplmayr, J.A. Lercher, Zeolites, 10 (1990) 283.

[232] C.V. Hidalgo, M. Kato, T. Hattori, N. Niwa and Y. Murakami, Zeolites, 4 (1984) 175.

[233] M. Guisnet, N.S. Gnep, H. Vasques and F. Ramôa Ribeiro, Stud. Surf. Sci. Cat., 69 (1991) 321.

[234] M. Niwa, H. Itoh, Kato, T. Hattori and Y. Murakami, J. Chem. Soc., Chem. Commun., (1982) 819.

[235] M. Niwa, Y. kawashima and Y. Murakami, J. Chem. Soc., Faraday Trans. I, 81 (1985) 2757.

[236] M. Niwa, S. Morimoto, M. Kato, T. Hattori and Y. Murakami, Proc. 8th Int. Congr. Catal. Berlin, Vol. IV, 1984, p. 701.

[237] M. Niwa, C.V. Hidalgo, T. Hattori and Y. Murakami, Stud. Surf. Sci. Catal., 28 (1986) 297.

[238] M. Niwa, M. Kato, T. Hattori and Y. Murakami, J. Phys. Chem., 90 (1986) 6233.

[239] T. Hibino, M. Niwa and Y. Murakami, J. Catal., 128 (1991) 551.

[240] T. Hibino, M. Niwa and Y. Murakami, Zeolites, 13 (1993) 518.

[241] T.C. Tsai and I. Wang, Appl. Catal., 77 (1991) 209.

[242] P. Ratnasamy and S.K. Pokhriyal, Appl. Catal., 55 (1989) 265.

[243] W.W. Kaeding, C. Chu, L.B. Young, B. Weinstein and S.A. Butter, J. Catal., 67 (1981) 159.

[244] M.A. Uguina, J.L. Sotelo, D.P. Serrano and R. Van Grieken, Ind. Eng. Chem. Res., 31 (1992) 1875.

[245] O.O Parenago, O.E. Lebedeva, I.I. Ivanova, N.E. Vil'yareal', L.E. Latysheva, S.A. Skornikova, V.V. Chenets and E.V. Lunina, Kinet. Katal., 34 (1993) 183.

[246] E. Benazzi, S. De Tavernier, P. Beccat, J.F. Joly, Ch. Nedez, J.-M. Basset and A. Choplin, Symposium on Chemical Modified Molecular Sieves, 206th National Meeting, ACS, Vol 38, N.3, Chicago, 1993 p. 561.

[247] S. Namba, A. Inaka and T. Yashima, Zeolites, 6 (1986) 107.

[248] J.R. Anderson, Y.F. Chang, A.E. Hughes, Catal. Lett., 2 (1989) 279.

[249] J.M. Silva, M.F. Ribeiro, F.Ramôa Ribeiro N.S. Gnep, M. Guisnet and E. Benazzi, React. Kinet. Catal. Lett., 54(1) (1994).

[250] I. Neves, F. Jayat, P. Magnoux, G. Perot, F. Ramôa Ribeiro, M. Gubelmann and M. Guisnet, J. Chem. Soc., Chem. Commun., 6 (1994) 717.

[251] D. Corbin, M. Keane, Jr., L. Abrams, R.D. Farlee, P.E. Bierstedt and T. Bein, J. Catal., 124 (1990) 268.

[252] M. Guisnet and P. Magnoux, Appl. Catal., 54, (1989) 1.

[253] P. Dejaifre, A. Auroux, P.C. Gravelle, J.C. Vedrine, Z. Gabelica and E.G. Derouane, J. Catal., 70 (1981) 123.

[254] W.W. Kaeding, Y. Brewster and C. Chu, J. Catal., 89 (1984) 267.

[255] R.M. Barrer, H. Villiger, Z. Kristallogr., 128 (1969) 352.

[256] J.A. Martens, H. Geerts, P.J. Grobet and P.A. Jacobs, in E.G. Derouane et al. (Eds.), Zeolite Microporous Solids: Synthesis, Structure and Reactivity, NATO ASI Series C 352, Kluwer Academic Publishers, Dordrecht, 1992, p. 477.