

## Review

# Zeolitic materials as catalysts for organic syntheses

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The major applications of zeolitic materials are as cation exchangers, selective adsorbents, catalysts and catalyst supports (mainly in catalytic cracking, hydroisomerization and aromatics processing). Their use in the synthesis of hydrocarbon intermediates and fine chemicals is at an earlier stage of research, although several international reunions and reviews have already shown the improvement achieved by using these solids in conventional catalytic processes. This improvement is found mainly in activity, selectivity and environmental concerns, new more environmentally friendly routes having been found for processes which previously produced undesirable side reactions or high amounts of environmentally hazardous residues (with the subsequent economic considerations). More than a hundred references form the main body of the present piece of work, which has three major objectives, the first of which is to outline the main properties of zeolitic materials in relation to their use as catalysts in organic syntheses, the second to present an up to date bibliographic review of their use for such purposes and the third to show the main improvements that these materials present with respect to the more conventional catalysts.

## 1. Introduction

The organic chemicals industry is based on the manufacture and processing of a great number of compounds commonly encountered in our everyday environment. Their chemical formulae have, in many cases, several reactive groups and their production is consequently complicated and costly, the conditions of synthesis having to be carefully chosen in order to avoid undesirably high temperatures. The usual way of achieving this being to find an adequate catalyst.

Of the two types of catalysis (according to the number of phases present: homogeneous (one phase), heterogeneous (several, i.e. solid–gas, liquid–gas, etc.), the most convenient for these syntheses is the latter, where a finely divided solid catalyst is suspended in the liquid reaction medium, or in a fixed bed through which the reactant gases or liquids pass. The main reason for the choice of heterogeneous catalysis being the greater ease of recovering the catalyst, with the consequent important economic considerations of the industrial processes (i.e. avoiding the distillation step necessary in homogeneous processes, with liquid catalysts). One of the more interesting examples of the advancements in this respect is the substitution of traditional Lewis catalysts (i.e.  $\text{AlCl}_3$  diluted in the liquid reaction medium) by zeolites.

Although natural zeolites of molecular sieve type have been known to mineralogists for a long time, it was not until 1954, when Barrer (Linde laboratories)

synthesized zeolite A with inorganic mixtures and thermal hydrotreatment.

Zeolites are natural or synthetic aluminosilicates with several properties that make them very useful as heterogeneous catalysts, i.e. they have exchangeable cations in an amount equivalent to the tetrahedral aluminium of the network (which can be substituted by those of catalytic importance or by protons, with the consequent effects on the acidity of the material), their pores (with one or more sizes) have diameters close to molecular dimensions (0.3–1.0 nm, although some have been synthesized with pore sizes up to 1.2 nm) depending on the size of the cations exchanged (typical hydrocarbon dimensions: benzene 0.57 nm  $\times$  0.22 nm; *n*-hexane, 0.35 nm  $\times$  0.42 nm). Their hydrophilicity is related to the aluminium content, those with lower Si/Al ratios being more hydrophilic (i.e. zeolite ZSM-5 has an unusual hydrophobicity owing to its high Si/Al ratio, see below), with consequent potential applications in the separation of hydrocarbons and polar compounds, such as water and alcohols, and their crystallinity which gives them sites of high uniformity.

Zeolites were first used in the petrochemicals industry in the 1960s for oil refining [1–11]. The first synthetic zeolites were developed in the laboratories of the petroleum companies (Union Carbide, zeolites A, X and Y; Mobil, zeolites ZSM and from the 1960s to the 1980s a major portion of their use was related to this industry.

Already in the 1960s their broad potential in organic syntheses and their importance as catalysts for these processes were advanced by Venuto and Landis [7], and in the Eighth International Conference of zeolites (1989), two plenary lectures were dedicated to this subject [8]. This development is reflected in the enormous increase in the amount of work published on this subject, i.e., between 1947 and 1956 there were approximately 100 publications about zeolites reviewed in *Chemical Abstracts* only three of them related to organic synthesis, while between 1982 and 1986 more than 10 000 publications can be found and 3000 of them show their use for this purpose.

## 2. Structure, synthesis, properties and types of zeolitic materials

### 2.1. Structure

The first zeolites cited in the scientific literature were natural crystalline hydrated aluminosilicates whose structure consisted of a three-dimensional network of  $\text{SiO}_4^{4-}$  and  $\text{AlO}_4^{5-}$  tetrahedra bonded by common oxygens which can be represented by the general formula  $\text{M}_{2/n}\text{O}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2\cdot y\text{H}_2\text{O}$ , where M is the charge-compensating cation, of valence  $n$ . There are more than 40 known natural zeolites and almost 200 synthetic ones. A great number of industrial processes are operated with zeolitic catalysts, although the number of zeolitic materials used as industrial catalysts is still mainly restricted to zeolite Y, mordenite and ZSM-5.

Fig. 1 shows two of the first zeolites discovered, with catalytic interest, zeolite A and zeolite Y. The basic building unit for these structures is referred to as sodalite, a truncated cubo-octahedron of 0.65 nm diameter, formed by  $\text{SiO}_4^{4-}$  and  $\text{AlO}_4^{5-}$  tetrahedra. When these sodalite units are joined by the four-member rings, zeolite A is obtained, and when joined by half of the six-member rings, zeolites X and Y are obtained (their difference being the Si/Al ratio).

Zeolite A [12] was the first synthesized with a complete structural characterization. It has a structure of interlinked channels with cavities, accessible through six "eight-member" rings, whose size makes possible the penetration of linear hydrocarbons into the interior of the structure but not of branched or aromatic species.

Zeolites X (and Y) have been widely used as catalysts and catalyst supports [13–18] for processes of fluid catalytic cracking and hydrocracking, due to their structure, which is formed by a central cavity, accessible through twelve-member rings, where linear as well as branched hydrocarbons can penetrate (typical hydrocarbon dimensions: benzene, 0.57 nm  $\times$  0.22 nm;  $n$ -hexane, 0.35 nm  $\times$  0.42 nm).

Fig. 2 shows two of the more catalytically useful zeolites ZSM-5 [19–22] and Mordenite [23, 24] (both of which are based on a unit which consists of a five-membered ring with one substituent).

In mordenite the subunits 5-1 are joined in chains forming two types of main channels, one restricted by twelve oxygens and the other by eight. This zeolite is commercially used in isomerization of light alkanes for octane enhancement of gasoline.

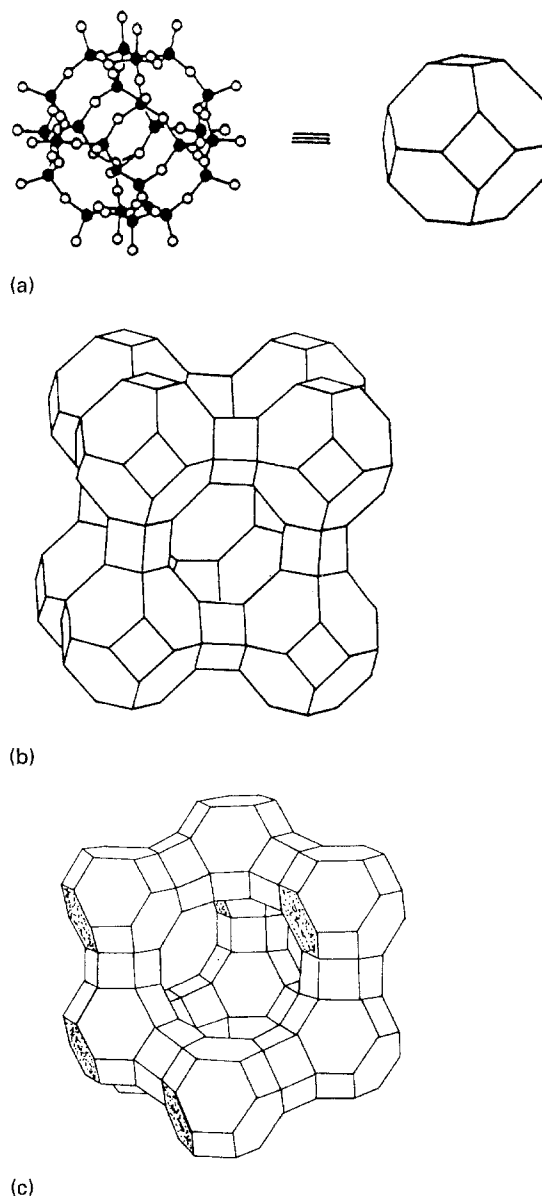


Figure 1 Zeolites based on sodalite units. (a) Structure of a sodalite unit. (b) Zeolite A. Pores: circular eight-member ring, main diameter 0.41 nm. Spherical cavities: main diameter 1.14 nm. Structural isotype: SAPO-42. (c) Zeolite Y (Faujasite). Pores: circular 12-member ring, main diameter 0.74 nm. Spherical cavities: main diameter 1.18 nm. Structural isotypes: zeolite X (zeolite Y: Si/Al > 2.5, zeolite Y: 1 < Si/Al < 1.5) and SAPO-37.

Zeolite ZSM-5 has two kinds of pores, the first consisting of zig-zag channels of quasi-circular section and the second of straight channels of elliptical cross-section. This zeolite has low aluminium content and consequently a low ionic exchange capacity. Its water content is also low, having a hydrophobic trend. Its crystalline structure was described in 1978, synthesized including organic molecules with nitrogen, such as tetrapropylammonium bromide in the reaction mixtures in preparations with very high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (20 to more than 8000), a second heat treatment being necessary to liberate the structure from the organic cation. This is the zeolite that has been more used in industrial processes, mainly for commodity petrochemicals and to produce gasoline from methanol. The titanium-containing analogue of ZSM-5 (TS-1) is employed for hydroxylation of phenol to mixtures of hydroquinone/catecol.

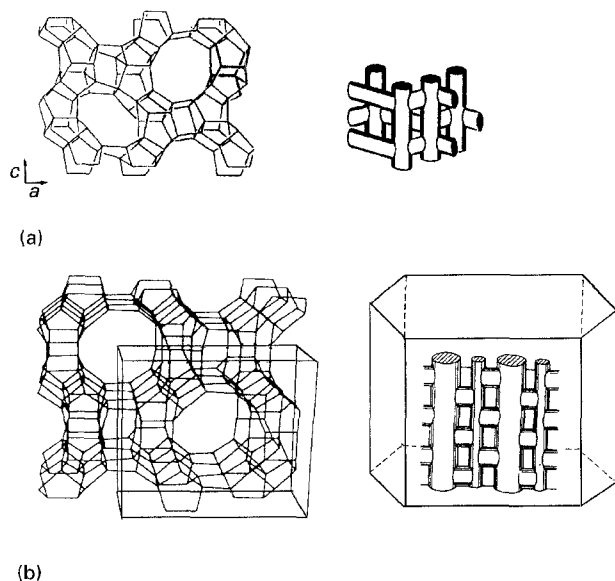


Figure 2 Zeolites based on 5-1 units. (a) zeolite ZSM-5. Pores: straight 10-member ring. Main diameters:  $0.52 \text{ nm} \times 0.57 \text{ nm}$  and sinusoidal  $0.53 \text{ nm} \times 0.56 \text{ nm}$ . Intersection cavities  $\sim 0.9 \text{ nm}$ . Structural isotypes: silicalite ( $\text{Si}/\text{Al} \approx \infty$ ), (Si, Ge)-MFI. (b) Mordenite Pores: straight 12-member ring  $0.7 \text{ nm} \times 0.65 \text{ nm}$  connected by eight-member rings ( $\sim 0.3 \text{ nm}$ ). Structural isotypes: high silica types  $5 \leq \text{Si}/\text{Al} \leq 20$ .

## 2.2. Synthesis

The starting point of the synthesis of zeolites is a crystallization at high pH ( $\approx 11\text{--}13$ ) from a mixture containing the sources of silicon and aluminium and water. There are many synthesis variables that can have an important influence on obtaining different zeolitic structures, for example, temperature, pressure, concentration, time, pH, aluminium, silicon, and cation sources.

The mechanism of formation of these compounds remains unknown to date, but it has been found that the species  $\text{Al}(\text{OH})_4^-$  is present in the synthesis solutions and has an important role in the process. The type of cations present is also important because they can have a templating effect on the forming structure [25], i.e. sodium cations facilitate the formation of structures based on subunits with double rings of six members. The use of voluminous organic cations (i.e. alkylammonium types [26–28]) can also influence the kind of structure obtained because channels of the zeolitic structure tend to form around the cation entities (see Fig. 3 below), or for example they can modify the gel chemistry by solubilizing one of the components (i.e. catechol dissolves silica), or modify the pH (i.e. the amines and quaternary ammonium hydroxides).

## 2.3. Properties

The main properties (with catalytic importance) of the zeolitic materials, are described below.

### 2.3.1. Molecular sieving ability

Zeolites can sieve a molecule from a mixture, because the openings of the zeolitic structure are of molecular

dimensions. Thus, diffusion in zeolites can be extremely restricted (configurational diffusion) with diffusion coefficients much lower than bulk or Knudsen diffusivities. Because of this, zeolites show an extraordinary selective reactivity, as some reactants and/or products cannot enter or leave the zeolite cavities because of their size or shape and/or bulkier transition states cannot be formed, these processes giving rise to the so-called shape selectivity (which can be of reactant, product or transition state type).

### 2.3.2. Cationic exchange capacity

The isomorphic substitution of silicon by aluminium gives rise to a net negative charge that is compensated for by cations, giving zeolites the property of cationic exchangers. The remaining space is filled by water molecules that can be desorbed by heating and evacuation, or replaced by a great number of organic and inorganic compounds. This property allows the preparation of solids of controllable and gradually changing properties, which can be extremely useful when working with reactions where slight increases in a property can lead to major changes in the catalytic behaviour.

### 2.3.3. High surface area

The apparent specific surface area of these solids is typically of the order of  $500\text{--}700 \text{ m}^2 \text{ g}^{-1}$ , measured in the conventional way (with nitrogen and analysis by the BET method [29]). This high value becomes particularly important when considering properties proportional to the surface area, as occurs in many cases with the catalytic ones. This area is mainly internal, because the particle sizes of the zeolitic materials are in the range of micrometres and therefore normally only 10% or less of the total surface area corresponds to the external surface area of the crystallites.

The nitrogen isotherms are of Type I and the extrapolation of the straight part of the isotherm to zero pressure does not represent the formation of a monolayer, but the volume filling of micropores. The use of the BET method of the characterization of the surface area is not completely correct, because it is based on the supposition of multilayer formation, and given the size of the nitrogen molecule ( $\approx 0.4 \text{ nm}$  diameter) and the pore size of the compounds under consideration, this is physically impossible. However, the method still gives a good fingerprint of the system.

The adsorption of nitrogen can also be analysed by Langmuir's method [30], in which the heat of adsorption is assumed to be constant with coverage. However, in many cases it has been found that the experimental data obtained on these solids do not agree with this theory.

Another theory that has been used is that of Freundlich, which assumes the exponential diminution of the heat of adsorption with coverage [31], but no success has been obtained in its application to these solids either.

Recently, a combination of both Langmuir's and Freundlich's theories has been used successfully for

analysing the data of adsorption of *p*-xylene on a ZSM-5 zeolite [32].

### 2.3.4. Variable acidity

The total acidity depends on the amount, strength and position of the acid sites present and can be varied by controlling the Si/Al ratio during the synthesis of the zeolites or in subsequent treatments, the most well known of them being dealumination (see Section 2.3.5).

Brönsted as well as Lewis, acid sites can be found in these structures [33]. Brönsted acid sites are the protons bonded to the oxygen atoms of the network and can be generated by exchange with acid solutions, thermal decomposition of ammonium ions, dissociation of the water molecules present in the structure under the strong electrostatic field of the cations, etc. Lewis acid sites are mainly due to the charge-compensating cations, or the trigonal aluminium atoms deficient in oxygen, and can be generated by dehydroxylation of two hydroxyl groups.

The process used to measure the acidity of these materials is based on the adsorption-desorption of ammonia and other bases of increasing size, their complementary use allowing the study of the whole zeolitic structure (intra- and extra-porous). For example, ammonia can reach inside the complete structure of the Y zeolite, while piridine cannot enter the hexagonal prisms.

### 2.3.5. Stability

The chemical and thermal stability can be increased by gradual leaching of aluminium atoms from the network [34–37], by means of strong acid solutions, chelating agents, etc. This treatment also causes other variations in the structure, i.e. the acid properties (because the Si/Al ratio is altered) and the hydrophilic character of the zeolite decreases (when only silicon is present, the structure is hydrophobic, i.e. the zeolite called Silicalite, see Fig. 2a, in which the amount of aluminium is practically zero [34–37]). Another way of stabilizing the structure is by exchanging the zeolite with polyvalent cations (it must be remembered that on changing the size of the cations, the porous aperture of the materials also changes). This property allows the reproducible preparation and activation of catalysts based on zeolitic materials.

## 2.4. Zeotypes

The zeolitic behaviour is also exhibited by other compounds that contain different elements other than silicon and aluminium in their composition, i.e. germanium, boron, phosphorus (alumino-phosphates, silico-alumino-phosphates, metal-silico-alumino-phosphates, etc.) [38–44], these being referred to as zeotypes. In the text, this denomination will be used for the catalysts, which in some cases related to those with silicon and aluminium in their composition and in others for those with zeolitic properties but a different composition. Their syntheses are accomplished by two

methods, direct, or modification of the syntheses of existing zeolites. Computer simulations show that the number of substances possible with zeolitic properties are in the millions.

Three of the zeotypes of higher catalytic importance more used nowadays will be considered here, ALPOs and SAPOs (MeALPOs and MeSAPOs), Ga–Ge and Be–B and pillared clays.

The structures of several aluminophosphates (ALPO-5, ALPO-11 and VPI-5) are included in Fig. 3, together with the main pore openings of those compounds.

### 2.4.1. ALPOs and SAPOs (MeALPOs and MeSAPOs)

These structures have a framework based on aluminium and phosphorus (with or without silicon and metals), as the initials of their name indicate [38–45]. They tend to present three-dimensional or laminar frameworks. Quite often in their syntheses, templating agents are used that give rise to different zeotypes (i.e. tetrapropylammonium, cyclohexylamine, etc.). Those with aluminium and phosphorus (both trivalent) in the same amount (ALPOs) do not have a net charge and therefore do not possess ion-exchange capacity. Within this family, some materials have been identified, i.e. VPI-5 with one-dimensional channels of 18-member rings and an approximate diameter of 1.2 nm [43, 44] (see Fig. 3).

When silicon is introduced in the synthesis (SAPOs), its tetravalence gives rise to a net negative charge, and therefore ionic exchange capacity.

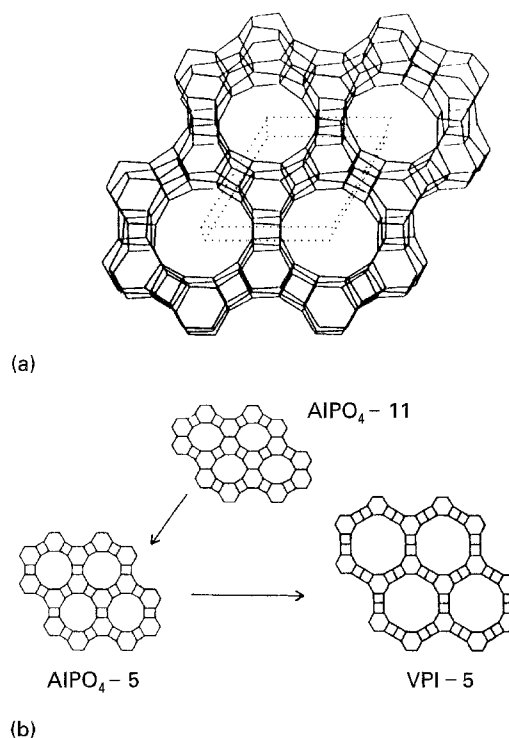


Figure 3 Structure of some aluminophosphates. (a) ALPO-5, Pores: straight circular 12-member ring. Main diameter 0.73 nm. Structural isotypes: SAPO-5. (b) ALPO-5 and ALPO-11. Pores: straight elliptic 10-member ring, main diameter 0.67 nm. VPI-5, pores straight quasi-circular 18-member ring, main diameter 1.2 nm.

On incorporating metals, the MeALPOs and MeSAPOs are encountered. In them the metal ion can substitute the phosphorus or the aluminium, with the corresponding change in properties, which can have important catalytic consequences, depending on the metal.

#### 2.4.2. Ga–Ge and Be–B structures

The similarities between gallium and aluminium and between germanium and silicon has induced research work in preparing zeotypes containing these elements (see Fig. 2a), the same occurring with beryllium and boron. As is the case with the ALPOs, and SAPOs, templating agents are also used in their syntheses.

The main structures studied up to the present are based on those of known zeolites with substitution by these elements (for the preparation of some boron-substituted zeolites, see [27, 28]).

#### 2.4.3. Pillared clays

Other structures that also present zeolitic behaviour are the pillared clays [45–47] (natural silicates with oxide entities intercalated between their layers), particularly important in those places where these kinds of natural materials are abundant and inexpensive (i.e. Spain).

Clays are aluminosilicates with particle sizes in the micrometre range, with ionic exchange capacity and mostly with laminar structures. They are formed of two different types of connecting layers, one of tetrahedra linked by the corners and the other of octahedra linked by their axis  $A(O, OH)_6$ , where A can be aluminium or other cations (i.e. magnesium).

Taking montmorillonite (layered structure) as an example, in it some of the aluminium of the octahedral sites is replaced by magnesium, leaving a residual negative charge, which can be compensated with cations. When water is added the structure swells due to the extra hydration of these intralaminar cations. At high temperature there is a collapse of the structure and the species are expelled from the inside of the intralaminar space. To prevent this collapse, pillaring of the structure has been developed. Pillars (organic or inorganic, but most commonly the latter) are introduced between the layers in order to keep the structure open, increase the thermal stability and leave, in this way, the interlayer space available for those compounds small enough to enter. These solids are similar to two-dimensional zeolites, with acidic and molecular sieve properties of considerable catalytic interest [48–52].

The pillaring process allows the production of families of microporous solids, because the porous structures formed between the galleries of the clay layers can be varied with the size and shape of the cation introduced. Some common pillaring species being the alkylammonium ions, metallic chelates and polyoximetallic cations.

### 3. Improvement of reactions of organic synthesis by using zeotypes as catalysts

As a summary of the above, it can be said that a zeolitic structure is that formed by a rigid framework whose composition can be converted between the hydrophilic and hydrophobic extremes (in the case of “Si/Al compounds, with alumination-dealumination” treatments), with exchangeable cations and strong acid sites (that favour the formation of carbonium ions) in well-defined positions of the network, with high and stable surface areas (with treatments that can be applied to increase the stability) and pore sizes close to molecular dimensions (which have given them the denomination of solid solvents).

The first area of application of zeolites was in reactions catalyzed by acid sites, via a carbonium-ion mechanism [53–56] (the major process being catalytic cracking, developed in the laboratories of the petrochemical companies, where these solids were first synthesized). However, recently other uses have been described in reactions via carbanions [57, 58] and free radicals [59, 60].

The property that makes zeotypes particularly useful as catalysts is the shape selectivity (see Section 2.3.1). In relation to this property, the surface area of the material and the structural stability become particularly important, as well as diffusional processes [61].

It has also been found that these materials have interest in relation to the activity outside the porous structure [62, 63].

Another important characteristic of these solids is that reactions which normally proceed through several steps can take place in only one step, owing to the proximity of reactive sites on their surfaces [64, 65], with the consequent saving of resources and energy. Examples of this property are given by the multifunctional zeolites, i.e. metal/zeolites.

Deactivation found in the catalysts based on zeolitic structures can be due to three main causes: coking, structural collapse or poisoning (i.e. by adsorption of bases on the highly acidic sites of the zeolitic structures). Nevertheless, their particular structure allows a low deactivation rate by coking, in comparison with more conventional catalysts, because of the steric hindrance of the formation of voluminous compounds inside the zeolitic cavities.

Many organic syntheses have been carried out with these catalysts, at least at a basic research level, and their prospects are certainly exciting, i.e.

(a) *isomerizations*: of double bond with acidic or basic zeolites [66], skeletal [67] and pinacol rearrangement [68];

(b) *electrophilic substitutions*: alkylations [69], acylations [70] and nitrations;

(c) *oxidations*: with oxygen [73], ammoxidation [74], with hydrogen peroxide [75] and with nitrous oxide [76];

(d) *cyclizations*: Diels–Alder cycloadditions [77, 78] and anthracene formation [79];

(e) *nucleophilic substitutions and additions*: addition of ammonia and amines to olefines [80], synthesis of

anilines [81] and addition of phosphines to olefines [82];

(f) *multistep syntheses*: hydroformulation [83, 84], hydrolysis and hydrogenation [85].

(For a widespread reference to the use of zeolitic materials in organic syntheses, the reader is referred to [6] Ch. 16.)

Several examples follow, which have been chosen in order to show how the structural characteristics of these types of substances influence their catalytic behaviour and present appreciable improvements with respect to conventional catalysts.

### 3.1. Avoidance of environmental drawbacks with respect to the traditional process

The industrial catalytic oxidation of ethylene to acetaldehyde with dioxygen was first reported in 1959 [86], using concentrated chloride solution of Pd(II) and Cu(II). The reaction mechanism is an electron-transfer chain by which electrons are transferred from ethylene over palladium and copper ions to dioxygen. Some technical and environmental drawbacks of this process are the use of very low pH, high chloride concentration and the formation of chlorinated byproducts.

Espeel et al. [87] have reported recently the preparation and catalytic activity in this reaction of a heterogeneous catalyst Cu–Pd–zeolite with the active centre being a partially ammoniated Pd(II) ion which belongs to an electron-transfer chain consisting of the alkene reagent, the zeolite encaged Pd<sup>II</sup>/Pd<sup>0</sup> and Cu<sup>II</sup>/Cu<sup>I</sup> redox couples and dioxygen. They compared the activity of a series of zeolites Y (with different Si/Al ratio) and found a synergistic effect between the copper and palladium (palladium zeolite has an initial activity at least five times lower than the same zeolite with Cu<sup>II</sup> and Pd<sup>II</sup> in atomic ratio of 2/1), and the activity of the catalyst is determined by the type of zeolite (ratio Si/Al), the cation density, and the presence of two amine ligands per palladium ion.

### 3.2. Shape selectivity towards reactants [88–90]

The complex Pd(II) bisalicylidene ethylene diamine is an effective catalyst in the homogeneous hydrogenation of alkenes, but it shows very low selectivity. Here the hydrogenation of linear and cyclic alkenes, using the Pd(II) complex in solution (conventional method) and embedded inside the cages of zeolites Y (or X), is compared.

The physical impossibility of the cyclic hydrocarbon to reach the active centre in the heterogenized catalyst, because its size is greater than the opening of the zeolite pores, makes the heterogenized catalyst very selective for the hydrogenation of linear hydrocarbons in linear-cyclic mixtures (typical hydrocarbon dimensions: benzene, 0.57 nm × 0.22 nm; *n*-hexane, 0.35 nm × 0.42 nm).

### 3.3. Shape selectivity of the transition state

The catalytic oxidative cyclization of 1, 5-dienes is a method for preparing mono- or bi-cyclic five-membered ring systems [91], a kind of carbocycles, which

mainly in their monochiral form are present in many biologically active compounds (i.e. prostaglandins, pheromones and terpenes). It was found that *cis*-1, 2-divinyl-cyclohexane can be oxidatively cyclized with moderate diastereoselectivities to bicyclic indanol esters when chiral acids are employed as nucleophiles instead of acetic acid [92].

In this work it is shown how the addition of zeolite 13X improves the diastereoselectivity of an oxidative cyclisation (17%–62%), because the zeolite adsorbs the diene and/or the acid, altering the energy differences between the two diastereoisomeric transition states and changing, in this way, the diastereoselectivity of the process.

### 3.4. Shape selectivity of the products

#### 3.4.1. Shape selective synthesis of 2, 6 di-isopropilnaphthalene [93]

2,6 di-alkylnaphthalenes are useful as raw materials for the preparation of liquid crystals, used in electronic displays. In the alkylation of naphthalene, 2,6 isomers are difficult to obtain through conventional alkylation methods (Friedel-Crafts) because the eight hydrogen atoms of the structure of the naphthalene can easily be substituted with alkyl groups and under the alkylation conditions, there can also exist other competitive reactions such as isomerization and transalkylation [94, 95]. Several zeolites were used in this work, including: zeolite Y, mordenite and ZSM-5 (see Figs 1 and 2).

The total activities in the alkylation reaction follow the order zeolite Y > mordenite >> ZSM-5. Zeolite ZSM-5 shows very low activity, because of its small pore size, lower than that of the reactants and therefore only its external surface is active. On the zeolite Y the selectivities obtained are similar to those of the homogeneous process, with about twice the amount of isomer 2,7-DIPN compared to the 2,6-DIPN (di-isopropyl naphthalene), because the size of this zeolite's pores does not impose enough restriction on the intermediates of reaction to change the selectivity.

However, on Mordenite, the amount of isomer 2,6-DIPN doubles compared with the 2,7-DIPN, because, as can be seen with volumetric models of both compounds, the structure of the 2,6-DIPN is more linear and consequently has less steric hindrance inside the straight channels of this zeolite than the 2,7-DIPN, thus affecting the final selectivity.

#### 3.4.2. Synthesis of dimethylamines

Methylamines are of considerable technical importance [96–99], being normally produced by reaction of methanol with ammonia on heterogeneous acid catalysts (using alumina as a catalyst). In many cases high amounts of the more useful dimethylamine (DMA) are desired, but in the homogeneous process normally the equilibrium mixture is obtained and with the heterogeneous process low selectivity to the DMA is shown.

By using zeolites as catalysts the selectivity to DMA has been increased to more than 70%, because the

steric hindrance of the TMA inside the porous structure does not favour the formation of this more voluminous compound.

### 3.5. Proximity of metallic and acid sites: lower deactivation rates

Conventional platinum-containing catalysts dehydrogenate propane but during this process there is a high coke deposition [100] (especially in the absence of hydrogen). The reaction mechanism consists of conversion of propane to propene on the metal sites and further oligomerization on the acid sites. The proximity of both types of site, which is of maximum importance, is easily achieved when zeolites are used.

Using zeolite ZSM-5 as the support for the platinum, the deactivation rate is much lower than with conventional catalysts, because the formation of coke is avoided inside the cavities, due to their size. Also, the size of the metallic particles inside the zeolitic structure is controlled by the size of the pores, and because the size and structure of metallic particles has an influence on their activity and selectivity, it influences the reaction characteristics, especially in structure-sensitive reactions [101–103].

### 3.6. Effect of the Si/Al ratio

The reaction of toluene with methanol on ZSM-5 gives *p*-xylene in the temperature range 593–743 K [104]. The *p*-xylene yield increases with increasing Si/Al ratio, in the range 11–500. The relation of these values with those of acidity measurements indicate that the stronger acid sites are more selective to the production of *p*-xylene.

### 3.7. Base catalysis

This side of the catalysis by zeolites is still underdeveloped, in comparison to acid catalysis. It was recognized in the 1970s [105] that zeolites exchanged with large alkali cations, catalyse the side-chain alkylation of toluene with methanol or formaldehyde, rather than the ring alkylation of xylenes, which occurs with acid zeolites.

Latterly, the side-chain alkylation to styrene/ethylbenzene mixtures on faujasites (zeolites X or Y) exchanged with alkali cations, dehydrogenation of isopropanol to acetone and alkylation of methane, ethane, acetone or toluene with methanol have been defined as a base-catalysed reaction via carbanions [106–108].

Three methods have been developed to obtain base zeolites: exchange [107, 108], impregnation with alkali azides [109], and impregnation with alkali acetate followed by decomposition of the acetate at high temperature in air or helium [110].

Owing to the fact that sometimes it is difficult to distinguish between acid and base catalysis on zeolitic materials, Dessau [111] has proposed the conversion of 2,5-hexanedione as a test reaction which, depending on the products, allows this differentiation. On acid zeolites, 2,5-dimethylfuran is formed (at medium con-

versions), while on base zeolites, 3-methylcyclopentanone is found in a very high selectivity at conversions above 50%.

### 3.8. Photochemical transformations

Photochemical reactions can be altered if they are carried out inside the pores of an appropriate zeolite [112]. In the chosen example, the photochemical decomposition of alkanephones was studied in non-acidic forms of zeolites X, ZSM and beta. The intermediate biradical can stabilize into two directions, by cyclization to a cyclobutanol or by elimination to acetophenone and an olefin. In a liquid solvent such as benzene, the ratio elimination/cyclization is slightly higher than 1. When zeolite X is used, the same ratios are found as in solution, owing to its spacious pore system. In the ZSM zeolites, the cyclization is almost completely suppressed due to the restriction of the rotational motion of the central sigma bond in the radical, with the consequent affect on the selectivity of the process.

### 3.9. Catalysis by zeotypes

In the chosen example, the dehydrogenation of cyclohexane to benzene (at 550 °C) on chromium-pillared clays is compared with the activity of a commercial Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst [113], finding an appreciable improvement in the conversion on the pillared sample (with pores of 1.1 nm formed inside the clay structure by the pillaring procedure and high degree of chromia dispersion) with respect to that of the commercial catalyst. The activity of this chromium-pillared sample is 100% at the beginning of the reaction and decreases only to 90% after 2 h on stream, while the activity of the commercial catalyst is originally 62% and decreases to 30% after 2 h reaction.

## 4. Future prospects

The intrinsic properties of zeolitic materials outlined here and the chosen catalytic examples, are a clear indication of why they are amongst the front-line solid catalysts used in the 1990s for processes of organic synthesis.

Another area of future development is that of fine chemicals, where the main stopping point until now has been the need of zeotypes with adequate dimensions to house the bulky reactants, intermediates or products which are related to this chemistry. Nevertheless, this is already being achieved with the synthesis of new zeotypes with adequate pore sizes (i.e. VPI-5) [114].

One of the main goals still to be achieved in this subject is that synthetic organic chemists routinely employ zeolitic catalysts, in order to take advantage of those fields where research has proved these types of materials to be of great importance, and to explore new ones [115–118]. It is easy to envisage that future developments will have to be based on the cooperation between synthetic organic chemists with a knowledge of the organic syntheses characteristics, and

synthetic zeolitic chemists, with the ability to tailor structures for every need.

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Received 15 December 1994  
and accepted 15 March 1995