



Review

Inorganic molecular sieves: Preparation, modification and industrial application in catalytic processes

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ABSTRACT

The increasing environmental concern and promotion of “green processes” are forcing the substitution of traditional acid and base homogeneous catalysts by solid ones. Among these heterogeneous catalysts, zeolites and zeotypes can be considered as real “green” catalysts, due to their benign nature from an environmental point of view. The importance of these inorganic molecular sieves within the field of heterogeneous catalysis relies not only on their microporous structure and the related shape selectivity, but also on the flexibility of their chemical composition. Modification of the zeolite framework composition results in materials with acidic, basic or redox properties, whereas multifunctional catalysts can be obtained by introducing metals by ion exchange or impregnation procedures, that can catalyze hydrogenation–dehydrogenation reactions, and the number of commercial applications of zeolite based catalysts is continuously expanding.

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In this review we discuss determinant issues for the development of zeolite based catalysts, going from zeolite catalyst preparation up to their industrial application. Concerning the synthesis of microporous materials we present some of the new trends moving into larger pore structures or into organic free synthesis media procedures, thanks to the incorporation of novel organic templates or alternative framework elements, and to the use of high-throughput synthesis methods. Post-synthesis zeolite modification and final catalyst conformation for industrial use are briefly discussed.

In a last section we give a thorough overview on the application of zeolites in industrial processes. Some of them are well established mature technologies, such as fluid catalytic cracking, hydrocracking or aromatics alkylation. Although the number of zeolite structures commercially used as heterogeneous catalysts in these fields is limited, the development of new catalysts is a continuous challenge due to the need for processing heavier feeds or for increasing the quality of the products. The application of zeolite based catalysts in the production of chemicals and fine chemicals is an emerging field, and will greatly depend on the discovery of new or known structures by alternative, lower cost, synthesis routes, and the fine tuning of their textural properties. Finally, biomass conversion and selective catalytic reduction for conversion of NO_x are two active research fields, highlighting the interest in these potential industrial applications.

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1. Introduction

Industrial catalysis and the corresponding catalytic processes have evolved during the last 250 years, and have become essential nowadays, with more than 90% of all industrial chemicals being produced by catalytic processes [1,2]. Catalysis is fundamental for a sustainable industrial society, where it accomplishes a double objective: environmental protection and economic profit. Improved catalytic processes will lower energy requirements, make a better use of natural resources, reduce the amount of subproducts formed and eliminate contaminant effluents. Heterogeneous catalysis provides additional advantages of easier separation and lower salt and waste production [3].

Among the heterogeneous catalysts it is safe to say that zeolites are the most widely used materials [4]. Besides their environmentally benign nature, the combination of a well-defined microporous structure with pore sizes in the range of molecular dimensions and a flexible chemical composition are key factors for their successful applications in fields as different as refining, petrochemistry or fine and speciality chemicals. The main properties of these solids are related to their topology and morphology, and chemical composition, that result in high surface area, the possibility of partitioning reactants from products, high adsorption capacity, possible modulation of the electronic properties of the active sites, and the presence of strong electric fields and confinement effects within the pores, which result in preactivation of the molecules. Last, but not least, zeolites present an outstanding thermal and hydrothermal stability [4].

Concerning their application as heterogeneous catalysts, the shape selectivity effects introduced by zeolites are of paramount importance. Indeed, their microporous channels, with dimensions in the range of many reactant molecules, provide zeolites with shape selectivity towards reactants, products or transition states [5]. The shape selectivity involving reactants and products is due to mass transport discrimination and is related to a true molecular sieve effect [6]. Transition state selectivity occurs when the geometry of the pores can stabilize one transition state among several possible. The implications of the fundamentals of shape selectivity on the development of catalysts for petroleum and petrochemical applications have been overviewed by Degnan in [7]. Despite the advantages that these shape selective properties confer on zeolites, as compared to other heterogeneous catalysts, they may become inadequate when processing reactants with molecular dimensions above those of the pores. Therefore big efforts have been made in order to increase the accessibility of active sites to larger molecules and to reduce the impact of diffusional problems on catalyst life. Possible approaches are: to synthesize extra-large pore zeolites [8–12], to decrease crystal size by direct synthesis [13–19] or by zeolite delamination [20], reducing in this way the length of the

diffusion path. Another way of decreasing the length of the diffusion path is to generate mesopores in the zeolite crystals by means of carbon templating [21,22], by chemical or steam postsynthesis treatments [23] or by the use of supramolecular templating [24].

Broadly, the zeolite production directed to catalytic uses is close to 20% of the total zeolite market, the rest being focused to detergents (70%) and adsorbents (10%) [25]. Despite these consumption data, catalytic applications are by far the largest in terms of market value, being this especially so in the oil refining industry. In fact, the catalytic cracking industry alone represents more than 95%, with a maximum catalyst cost of 5\$/kg. The rest accounts for specialty zeolites (20–30\$/kg), where the catalyst value depends not only on the zeolite synthesis and modifications, but also on the value of the final product [25,26].

Most of the current large scale commercial processes using zeolite based catalysts are in the petroleum refining and petrochemical industry [27]. Applications for the chemical industry involve mainly oximation, epoxidation, acylations, condensation and amination processes. Moreover, their presence is increasing in emerging fields such as environmental applications, the transformation of raw materials by means of non-conventional processes, such as coal, gas and oil conversion into syngas, olefins, acetylene and aromatics, all of them involved in value added chains, and conversion of methanol to propylene (MTP) and gasoline (MTG) [25]. Their potential application in the conversion of biomass is also gaining interest and has been recently reviewed [28].

If we compare the industrial application of acid and base solid catalysts, only 8% of the processes correspond to solid bases and none of these reactions, as far as we know, is performed with basic zeolite catalysts, although pilot plant trials were conducted in some cases [29–31]. An important handicap for the industrial application of basic zeolites relies on the fact that inexpensive NaOH and KOH are the competing catalysts. Their low cost and the easy processing of the residues formed, reduce the possibility of zeolite application to cases where special selectivity effects will be needed.

In this manuscript we will introduce some developments in the field of zeolites that go from synthesis and modification to their conformation as heterogeneous catalysts and application in commercial processes. The processes presented range from oil refining and petrochemicals to fine chemicals, and from conversion of alternative raw materials such as natural gas or biomass to the reduction of contaminants in stationary and mobile source emissions. Our aim has been to highlight the most recent advances in all these fields and to direct the reader to more specific revisions recently published.

2. Synthesis of inorganic molecular sieves

Increasing environmental concern and development of green processes based on heterogeneous catalysts are driving forces, not

only for the improvement of conventional zeolites but also for discovering new molecular sieves with novel pore architectures [9–11,25,32,33]. However, it is important to note that the well-established “big-five” zeolites, i.e. Y, ZSM-5, Mordenite, Beta and Ferrierite, are difficult to beat, due to their good performance and relatively low cost production, as they do not require the use of expensive or complex organic structure directing agents for their synthesis [34].

S.T. Wilson, in a very interesting overview concerning the new trends in zeolites synthesis, remarks on some of the strategies that have been successfully used in the discovery of 14 new frameworks during the period elapsed between the 14th and 15th edition of the International Zeolite Conference [35]. These strategies include the use of novel organic templates, the synthesis in F-media, the introduction of alternative framework elements (Ge, Be), and in some cases the use of high-throughput techniques for synthesis. A final approach for the synthesis of zeolites consists in the solid state topotactic transformation of layered structures into zeolites. Again, it is concluded that the commercial viability of a new structure will be determined mainly by its unique performance and production costs. We would like to highlight here a very interesting new avenue that involves the synthesis of zeolites that were previously carried out with organic structure directing agents, and can now be synthesized in an organic free synthesis media, though large amounts of seeds have to be used [36–40].

The need for expanding the application of zeolite based catalysts to processes involving bulkier molecules, has lead to different approaches into generation of larger pores and additional intra- or intercrystalline mesoporosity [24,41,42]. After establishing new starting hypothesis or after the synthesis of large libraries of organic structure directing agents (OSDA), the use of high-throughput (HT) synthesis techniques has been very useful for the discovery of new structures or for the optimization of existing ones. In the next section we will revise the application of high-throughput techniques to zeolite synthesis, and how they have lead to the discovery, among others, of a large number of extralarge pore zeolites.

2.1. Conventional vs. high-throughput systems for laboratory zeolite synthesis

The synthesis of zeolites is influenced by a large number of variables among which we can highlight different framework elements, mineralizing media, inorganic cations, and the use of organic or inorganic SDAs [43]. Traditional laboratory synthesis studies in which one variable is modified at a time, usually require long times to explore large regions within the synthesis phase diagram. Moreover, in the field of zeolite synthesis the prediction of a zeolite structure to be obtained under certain synthesis conditions cannot yet be achieved. Then, the application of high-throughput (HT) synthesis techniques combined with data mining reduces the screening time and optimizes the number of experiments to be conducted for exploring a given region of the synthesis diagram. Owing to this, the number of synthesis variables that can be studied at a higher level is larger, and this allows increasing the probabilities of finding new materials, while achieving a better understanding of the crystallization mechanisms, providing that clear starting hypothesis are made. Furthermore, the exploration of synthesis conditions out of the conventional ranges used in traditional studies is enabled. From a more applied point of view, high-throughput techniques may be useful for the search of alternative synthesis methods with reduced costs, and the increased rate of experimental learning and discovery will reduce the time-to-market of new or optimized catalyst technologies. In any case, the use of high-throughput strategies must never be considered as the substitute of a well planned approach [44–46], but one should always follow the

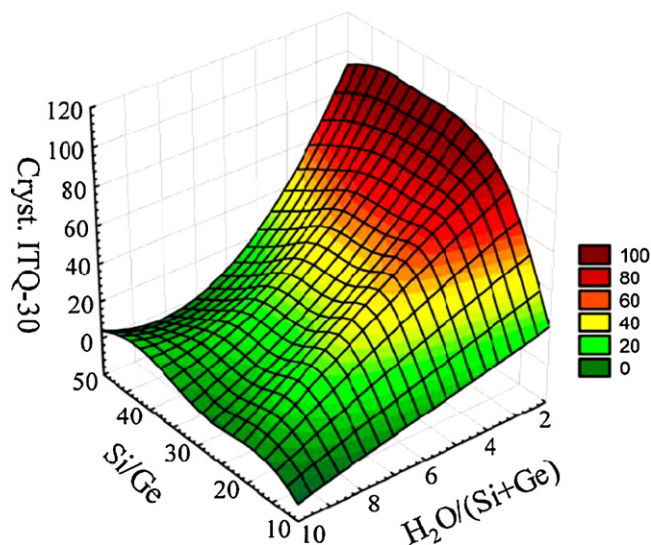


Fig. 1. Three-dimensional chart showing the evolution of ITQ-30 crystallinity. Synthesis conditions: 5 days; Al/(Si + Ge)=0.02; MSPTF/(Si + Ge)=0.5. Taken from [60], reproduced with permission of Elsevier.

scientific approach which can be now facilitated by the possibility of producing a larger number of results [47–49].

HT experimentation combines different elements such as the automated parallel synthesis of solids, the parallel physico-chemical characterization, fast sequential testing of some of their most interesting properties, and the use of data mining techniques to maximize the information acquired [50–54].

The Syntef group published the first report on a HT parallel zeolite synthesis in 1998 [55] and some years later Yu and co-workers discovered new zinc phosphate structures by means of a combinatorial approach [56]. HT methods were employed by Corma et al. for the discovery of zeolite ITQ-21, a very open 3-dimensional large pore structure, in a first approach [57], and for the optimization of the synthesis procedure and fine-tuning of crystallite size in a second stage [58,59]. ITQ-30 [60] and ITQ-24 [61] were also obtained and their synthesis optimized by means of a rational design of HT synthesis (Fig. 1) and characterization experiments, combined with the use of data mining techniques. A few years later a powerful data mining technique has been developed to be able to identify each individual zeolite structure in a synthesis product that contains several crystalline structures and still amorphous material [54,62].

Researchers from UOP have used the HT experimentation to explore the combination of commercially available templates in order to reduce the cost of potential new zeolite structures [63]. In this way zeolites UZM-4, UZM-8, UZM-15, UZM-17, or UZM-22, among others, were discovered [64,65]. In a first step a synthesis reaction mixture containing organoammonium hydroxides as SDAs is prepared where the charges between the organic SDA and potential framework to be formed are intentionally unbalanced. The controlled addition of alkaline or alkaline earth cations at low concentrations induces the crystallization of the structure, cooperating with the organic template.

In the last years the application of HT experimentation has led to the discovery of many interesting zeolites: ITQ-32 [66], ITQ-33 [8], ITQ-37 [9], ITQ-40 [10], ITQ-44 [67] or ITQ-47 [11]. ITQ-32 is a bidirectional zeolite with 8R pores connected by 12R channels which can be prepared as a nearly pure silica zeolite and as aluminosilicate. Its pore topology exhibits a unidirectional small 8R channel system along the *a*-axis, with a pore aperture of $3.5 \text{ \AA} \times 4.3 \text{ \AA}$, crossed perpendicularly by short 12R channels with a diameter of 6.3 \AA and 16.2 \AA in length [66]. Zeolite ITQ-33 is a silicoaluminoger-

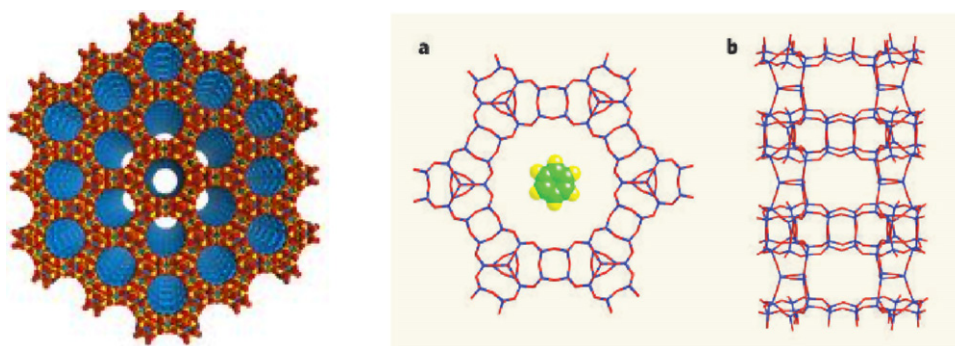


Fig. 2. ITQ-33.

Taken from [8]. Reproduced with permission of Nature Publishing Group.

manate whose structure exhibits straight large pore channels with circular openings of 18-rings along the *c* axis interconnected by a bidirectional system of 10-ring channels (see Fig. 2). The high-throughput techniques used in that study allowed the identification of its synthesis conditions, which are easily accessible, but not typical [8].

The combination of its unique structure with the successful incorporation of Al in framework positions resulted in an acid zeolite with interesting catalytic properties. When used for catalytic cracking of a vacuum gasoil it was able to increase simultaneously the yields to the highly valuable propylene and butenes and to the diesel fraction [8,68], while decreasing the yield of gasoline.

The structure of ITQ-33 was already predicted by Foster and Treacy by computational simulation as a thermodynamically feasible structure [69]. The same database predicted a zeolite topology with a $18 \times 12 \times 12$ -R pore system containing double 3-ring units. The synthesis of this structure has been recently achieved as a silicogermanate (ITQ-44) by using a rigid, bulky and relatively unexpensive SDA, working in fluoride media and using HT synthesis techniques [67]. ITQ-40, an extralarge pore zeolite containing D3-Rs and D4-Rs has also been discovered recently [10]. Interestingly the pore structure is formed by $15 \times 16 \times 16$ -member ring channels, and has the lowest framework density of all existing 4-coordinated oxide frameworks, 10.1 T atoms per 1000 \AA^3 .

The systematic exploration of the phase diagrams of germanosilicates by high-throughput techniques using three large dicationic organic structure directing agents was the key for discovering the new zeolite ITQ-37 [9]. ITQ-37 is a germanosilicate zeolite with extralarge 30-ring windows and pore size dimension within the mesoporous range, and it is the first chiral zeolite with a single gyroidal channel.

As we have seen, HT experimentation has demonstrated to be a powerful technique in zeolite synthesis research and is expected to be increasingly implemented in most laboratories working in this field.

2.2. Role of structure directing agents

Organic cations were first introduced in the zeolite synthesis by Barrera and Denny [70], with the aim of increasing the Si/Al ratio of the final materials. In this way ZSM-5 and beta, defined as high-silica zeolites, were obtained [71,72]. Since then the introduction of organic templates has been one of the main drivers in the synthesis of new zeolite structures [35,73], especially when the synthesis of high silica materials or aluminophosphates were the objective, and an historical revision on the trends in the use of organic structure directing agents (OSDA) in zeolite synthesis has been recently published by Burton and Zones [74].

While important advances have been made, the exact role of the SDA in the zeolite synthesis is not yet fully understood. The encapsulation within the microporous structure points out to, at least,

some control on pore architecture and stabilization of the system, due to weak as well as electrostatic interactions between the framework and the occluded organic species. However, in general, SDAs are not as specific as expected, and the same organic molecule can lead to different zeolite structures depending on the experimental conditions [75]. It is known that, besides the influence of the SDA, the presence of certain inorganic cations (alkalines, Zn, B, Ge) in the synthesis gel, or the use of fluoride anions as silica mobilizing agents, can also direct certain structural features, and will therefore promote specific structures.

A nice example of how the use of organic molecules can help increasing the Si/Al ratio of a certain zeolite is the evolution of zeolite A (LTA). Traditionally, this zeolite was synthesized with a Si/Al ratio of 1. The incorporation of TMA increased the ratio to values of 3 and by combination of TMA with the bulkier tetraethylammonium cations, UOP researchers synthesized UZM-9, a LTA structure with Si/Al ratio up to 9 [74]. Recently a LTA Ge-containing zeolite with a (Si+Ge)/Al ratio of 80, as well as the pure silica and Ge free LTA structure, has been synthesized in fluoride media and has been named zeolite ITQ-29 [76]. Interestingly, a rigid multi-cyclic quaternary ammonium compound was used as SDA that is able to self-assemble in solution forming a supramolecular complex, which fits perfectly within the alpha-cage of the LTA structure (see Fig. 3).

When TMA cations, which stabilized the sodalite units and also balanced the charge excess due to the fluoride anions within the D4R, were added to the synthesis media together with the bulkier OSDA, the pure silica LTA zeolite (ITQ-29) was produced. One of the most interesting applications of this Al free LTA, highly stable and hydrophobic, could be gas separation in the presence of H_2O or other polar molecules [76].

The use of phosphonium (instead of ammonium) based OSDA has allowed the synthesis of new structures (ITQ-27 [77], ITQ-34 [78]). Moreover, the use of phosphazenes has allowed the synthesis of the elusive Boggside zeolite [11]. This material (ITQ-47), known up to now only in its natural form, presents a bidirectional microporous channel system formed by 10 and 12MR pores. The use of P-containing SDA has also enabled the improvement of the synthesis of ITQ-27, increasing the range of Si/Al ratio possible [79]. Moreover, the P stabilizes the zeolite structure towards hydrothermal treatment simulating regeneration conditions during FCC process [80].

The group of Morris has recently presented the synthesis of zeolites and other microporous materials in ionothermal media [81–84], and a complete review on this topic can be found in [85]. It is presented that the ionic liquids can play a double role, as solvent and as SDA.

Initially only ALPO materials could be obtained following this procedure (see Fig. 4 for some of the structured obtained), due to

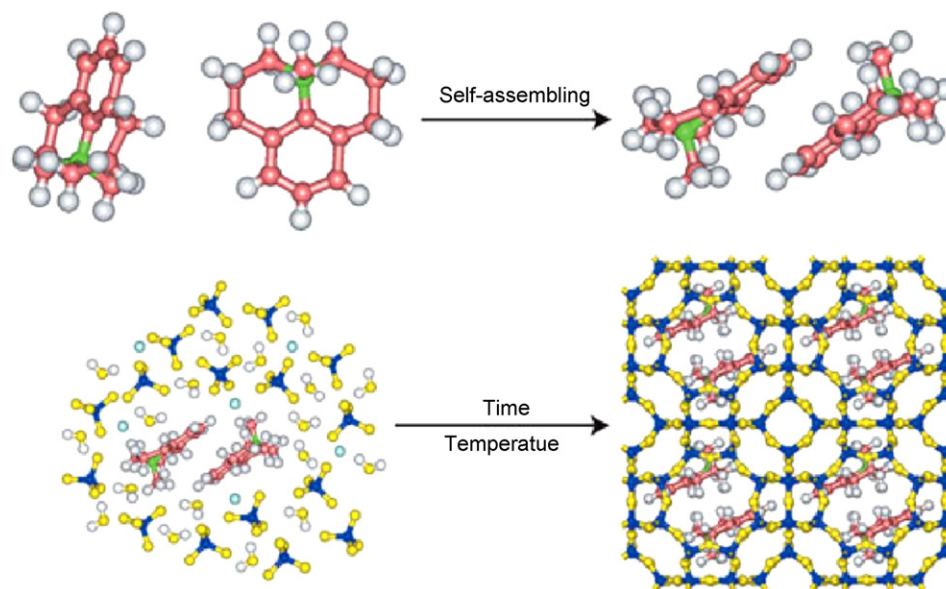


Fig. 3. Self-assembling SDA used for synthesis of ITQ-29 (high silica LTA). Taken from [76]. Reproduced with permission of Nature Publishing Group.

the limited solubility of the silica precursors, which is below the required for the synthesis of silico-aluminates. Recently this group succeeded in the synthesis of pure silica TON and MFI zeolites in an ionic liquid media by adding bromide–hydroxide, that increases the solubility of the silica precursors and enables zeolite crystallization in reasonable times. The use of ionic liquids as solvents allows high temperatures at ambient pressures. However, due to

the high temperatures used, the ionic liquid can decompose, and the decomposition products may play a decisive role for the synthesis, as described in [82]. Regardless of economic issues, the use of synthesis media others than water may open the possibility for new microporous structures to be discovered.

The cooperative structure directing effects in the synthesis of crystalline molecular sieves when using more than one template has been recently reviewed by Pérez-Pariente et al. [86]. His group has explored the combination of bulky and small SDAs for modifying the accessibility of the Brønsted acid sites in ferrierites. When using 1-benzyl-1-methylpyrrolidinium (bmp) and the cage forming TMA (see Fig. 5) they observed both molecules participate simultaneously in the crystallization of the FER structure [87–89].

Moreover, varying the combination of TMA, pyrrolidine and bmp results in different distribution of the bridging hydroxyls responsible for the catalytic activity [90] located in the ferrierite cage, accessible through 8MR windows, and the 10MR channels. Accessibility of the active acid sites was measured by FT-IR combined with pyridine adsorption, and the implications on the catalytic activity have been indicated.

UOP researchers have described that the cooperative templating between a large organocation with low charge density and a small organocation with high charge density (TMA) enables the synthesis of zeolites with lower Si/Al ratios. This concept is known as the charge density mismatch [91].

Another approach presented by Lee et al. [92,93] is the use of ketal-containing SDA. These molecules can be disassembled and reassembled easily enabling their removal from the microporous structure without the need of calcination (see Fig. 6).

The SDA molecule occluded in the zeolite structure is chemically cleaved into fragments that can be extracted from the microporous channel system and finally recombined to form the original SDA. This general methodology has proven to be adequate for the synthesis of ZSM-5, VPI-8, and ZSM-12.

Organic functionalization of microporous zeolites for broadening the diversity of catalytic active and shape selective sites is not straightforward. In fact, if the organic functions are incorporated by post-synthesis grafting, most of them will be located at the external surface of the crystals, and will therefore present no shape selectivity. Jones et al. developed in the late 1990s a direct synthesis

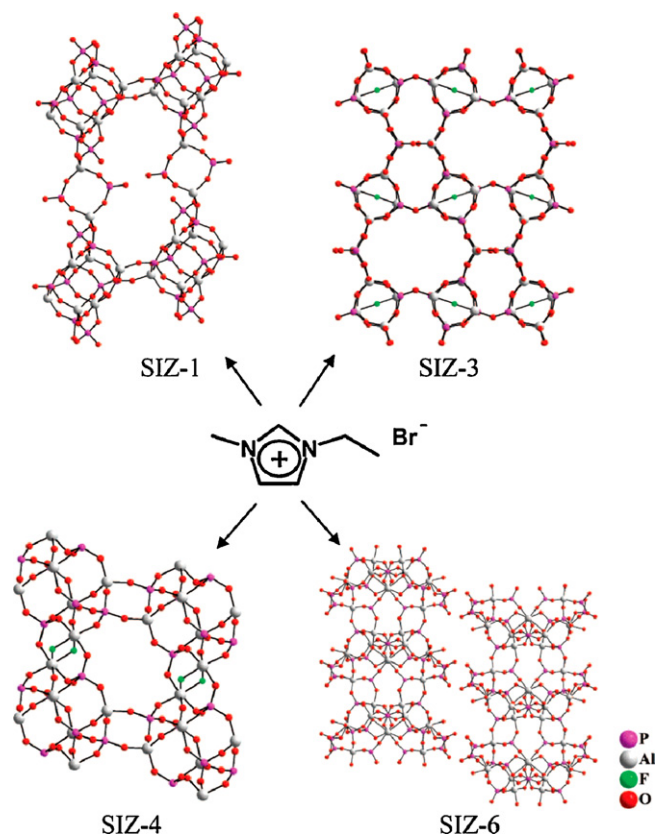


Fig. 4. Ball-and-stick diagrams of the ionothermally synthesized aluminophosphates SIZ-1, SIZ-3, SIZ-4, and SIZ-6. The SDAs have been omitted for clarity. Taken from [82]. Reproduced with permission of ACS.

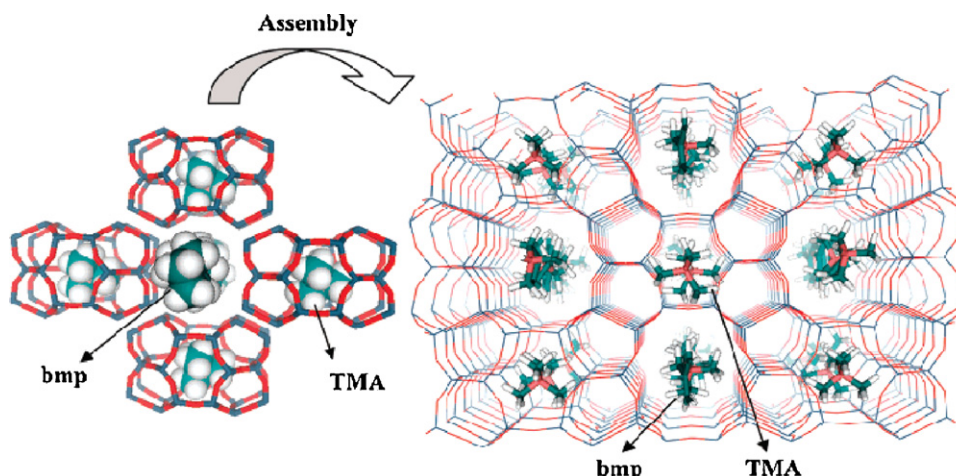


Fig. 5. Scheme of the self-assembly of TMA-filled cavities around bmp molecules to give the final ferrierite structure. Taken from [87]. Reproduced with permission of ACS.

method for obtaining organic-functionalized molecular sieves (OFMSs) with BEA structure [94–97]. The OFMSs were prepared using tetraethylammonium fluoride as SDA, and different functional groups (phenethyl, cyanoethyl, iodopropyl, bromopropyl, allyl, dimethylaminopropyl, and mercaptopropyl) were covalently bonded to framework silicon atoms by adding the corresponding organosilane into the zeolite synthesis gel. When evaluating the catalytic behavior of these type of materials, two competing effects have to be considered: the activity will be proportional to the number of active sites, but an increase of the active organic functions will result in increasing diffusional limitations [97].

The possibility for preparing zeolite single layers was demonstrated by delaminating layered precursors of zeolites by means of post-synthesis treatments (see Fig. 7). In this way zeolites ITQ-2 [20,98], ITQ-6 [99,100], ITQ-18 [101] and ITQ-20 [102] have been prepared. The resultant zeolitic materials showed very high accessible surface areas and interesting catalytic properties for a large number of acid catalyzed reactions [103–111].

Moreover, the single layers have been used to form hybrid organic–inorganic materials, as shown in Fig. 8, with a combination of micro- and mesopores that allow the preparation of bifunctional acid–base catalysts [112].

Very recently Ryoo et al. have obtained single layers of zeolite ZSM-5 by direct synthesis. This has been achieved by using large organic molecules with diquaternary ammo-

nium groups located at the end of the chain. Indeed, $C_{22}H_{45}-N_1(CH_3)_2-C_6H_{12}-N_1(CH_3)_2-C_6H_{13}$ is composed of a long-chain alkyl group (C_{22}) and two quaternary ammonium groups spaced by a C_6 alkyl linkage. The cationic groups act as SDAs to crystallize the ZSM-5 monolayers and the long hydrophobic chain limits their growth along the “b” direction, as shown in Fig. 9 [13].

2.3. Considerations for large scale commercial zeolite synthesis

Zones has recently presented a number of issues that need to be taking into account before considering a zeolite commercialization [113]. First, if organic SDA molecules are used, their price and their possible risks from the environmental and health point of view have to be considered. Safety issues on equipments and products are also important. Concerning the synthesis process itself, for commercial scale production of zeolites, synthesis time and post-synthesis steps have to be carefully evaluated. Finally, the waste streams generated and their possible treatment must be taken into account.

Schmidt [114] has presented a nice overview on the development of new technologies for solid catalysts preparation, including zeolite based catalysts, and their potential implementation from an industrial perspective. According to his analysis, the catalyst industry, which was technology driven, has become more and more dependent on cost, and cost reduction can be a limiting factor for both, manufacturer and catalyst user. The development of new production technologies involves high risks and important capital investment, and will only be considered if the benefits, from a performance, cost or environmental point of view are clear. On the contrary, the efforts will be directed to the improvement of existing technologies.

Some important advances have been achieved recently in zeolite synthesis that can reduce costs of known materials and/or facilitate the industrial application of other zeolites. The most relevant approaches are listed below:

- Organic-free zeolite synthesis. Some zeolites synthesized in the absence of OSDA are ZSM-34 [36,38], ZSM-12 [39], ECR-1 or beta [37,40]. A second generation of organotemplate-free beta has been presented recently (IZC-IMMS 2010) as “Green Beta”. The difference, as compared to the first generation, is that the beta seeds used here are also organic-free.
- Low effluent or dry hydrothermal synthesis. The main advantage of this procedure is the non-generation of a mother-liquor. However, if organics are used for the synthesis, they will be difficult to

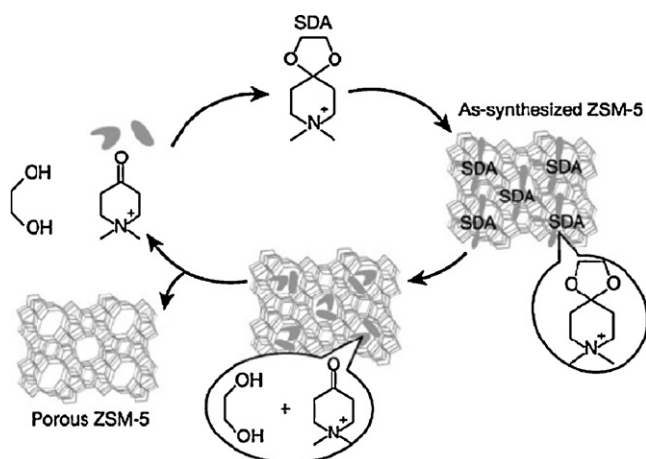


Fig. 6. Specific example using a cyclic ketal to give ZSM-5. Taken from [92]. Reproduced with permission of Nature Publishing Group.

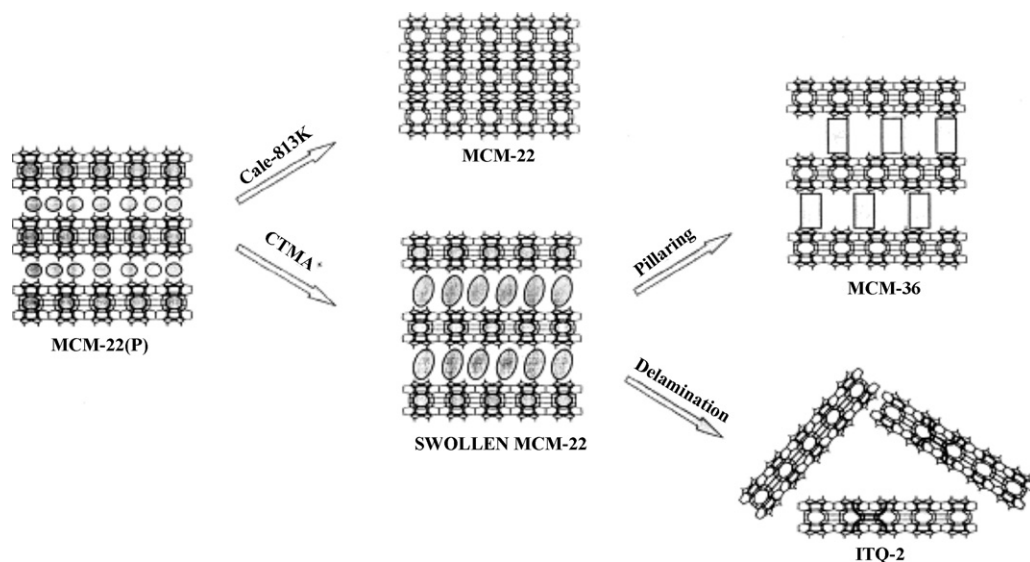


Fig. 7. Schematic representation of the preparation of MWW-type zeolite, MCM-36 and ITQ-2 from MCM-22(P). Taken from [98]. Reproduced with permission of Elsevier.

recover for recycling unless a washing or extraction step is performed, and then the main benefit of the method is lost. Moreover, manipulation of the dry paste and homogenization of the temperature profile during the synthesis are serious drawbacks for a large-scale commercial application. More details can be found in [114]. Hari Prasad Rao et al. described the preparation of high silica Beta zeolite by this procedure [115].

- Zeolite bound zeolites. Here an appropriate binder, mesoporous silica–alumina, is transformed into a zeolite via a secondary synthesis [116,117]. This novel procedure, assigned to Lummus Technology, has been demonstrated for some of the most demanded zeolites in the catalysts and adsorbents industry, e.g. beta, ZSM-5, mordenite, X, Y and A [118].
- Microwave zeolite synthesis [119,120]. The use of microwave heating results in energy and synthesis time savings.
- Zeolite synthesis using degradable structure-directing agents and pore-filling agents [92,93]. This approach, already presented in

the previous section, opens potential lower cost synthesis routes, as the expensive SDA molecules can be totally recovered under mild conditions and without the generation of harmful waste streams.

- Low cost zeolite production using waste fly ash or biomass ash as silica and/or alumina sources: ashes from different sources, such as fly ash during coal combustion or biomass ash, such as the one obtained by combustion of rice hull, will differ in their composition not only because of their different origin, but also depending on the combustion conditions [121,122]. However, they are all rich in silica and alumina, present as amorphous and/or crystalline phases and usually also contain Na. These solid waste products have been used as silica and alumina precursors for zeolites when dissolved in basic media, and single phases of zeolites A, X, Y, P1 and ZSM-5 have been described. However, none of the procedures described has found large scale application. One of the main drawbacks is that the complete conversion of ash into the crystalline zeolite is not achieved. Dissolution of the Si and Al precursors and crystallization of the zeolite are simultaneous processes, and the formation of zeolite crystals on the ash particles can limit further reaction. Moreover, fly ash is usually processed without prior purification, and remaining coal and impurities such as Fe₂O₃ may contaminate the final zeolitic product.

3. Post-synthesis modification of inorganic molecular sieves

Two very complete compilations on the most employed post-synthesis modifications of zeolites are given by Kúhl [123] and Szostak [124]. In a more recent study [125], Chen and Zones include two additional modification procedures: the substitution of the original T-atoms present in the as synthesized zeolite, such as B, by the desired atoms, usually Al or Si [126,127], and the preparation of highly crystalline hydrophobic pure-silica zeolites, such as CIT-1 and SSZ-33, by means of post-synthesis treatment of borosilicate zeolites with acetic acid [128].

Most of the zeolites in their as-synthesized form are not active, as their microporous structure is filled with organic molecules and/or inorganic species that will have to be removed by calcination or extraction of the organic agents or by ion-exchange procedures as in the case of substitution of alkaline cations by the active

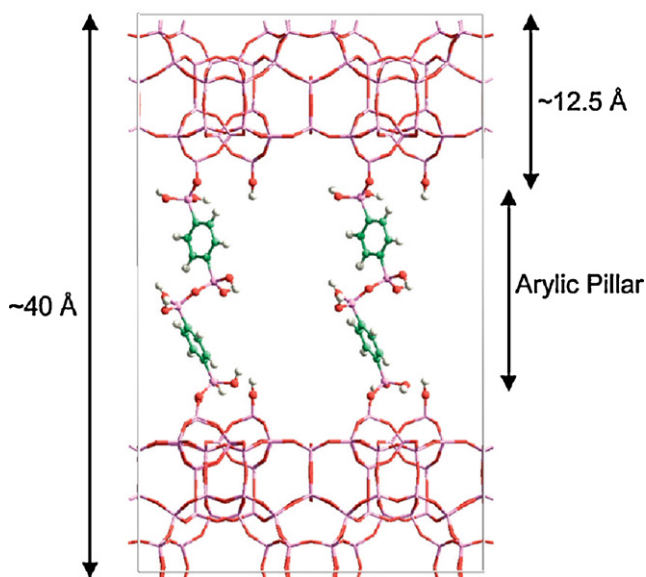


Fig. 8. Artistic representation of layered hybrid material obtained by pillaring with BTEB silsesquioxane molecules (MWW-BTEB). Taken from [112]. Reproduced with permission of ACS.

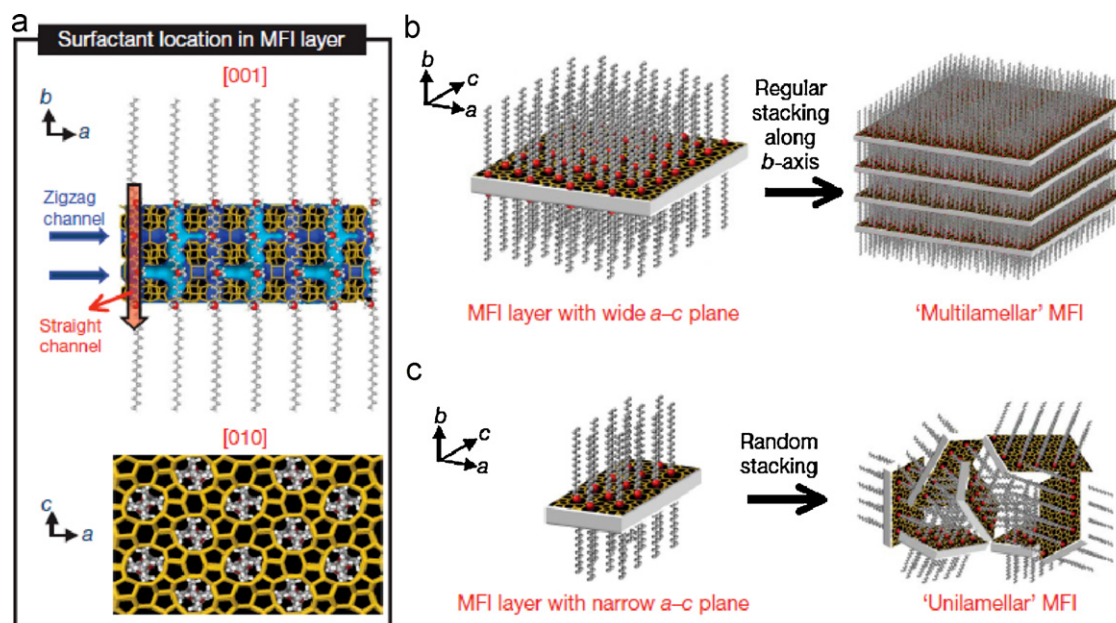


Fig. 9. Crystallization of MFI nanosheets. Taken from [13]. Reproduced with permission of Nature Publishing Group.

protons. These procedures can be enclosed in a first group of treatments that are necessary to activate the zeolite. Other modifications are directed to improve the thermal and hydrothermal stability of the framework, for example by dealumination of low Si/Al zeolites. A clear example is the ultrastabilization of the Y zeolite used as active component in catalytic cracking and hydrocracking processes [129]. The objective may also be to increase the accessibility to the active sites by generation of mesoporosity. Traditionally this has been achieved by combination of hydrothermal treatments and acid leaching, but in the last years alternative treatments in basic media have been presented to generate mesoporosity in high silica zeolites [130–134]. An extensive review on this subject has been recently published [42].

Sometimes the aim of the post-synthesis modification is to remove non-selective active sites located close to or at the external surface of the zeolite crystallites by selectivation processes. This can be achieved by dealumination of the external surface by treating the zeolite with bulky acids, such as oxalic acid, or by means of complexing agents such as EDTA, while acid treatment with stronger acids can be performed with the as synthesized zeolite when it still contains the organic inside of the channels. Selective coking is another option, used for example by Exxon-Mobil Chemicals and Shell for selective toluene disproportionation and production of *i*-butene from 1-butene, respectively. Most of these selectivation procedures have also been described in the early patent literature for oligomerization of light olefins to high cetane diesel [135,136]. The chemical vapor deposition (CVD) of silica on medium pore zeolites is also used for decreasing the number of non-selective external active sites and for regulating the size of the pore openings, improving in this way the para-selectivity in the production of di-substituted aromatics [137–140], or decreasing the deactivation rate in methane dehydroaromatization [141].

The activity of a catalyst can be greatly enhanced by fine-tuning the hydrophobic–hydrophilic nature of the material. In this line, important benefits have been observed by silylation of Ti-micro and mesoporous materials for olefin epoxidation catalysts. Silylation of the external surface results in a more hydrophobic catalyst and inhibits the undesired ring-opening of the epoxide [142,143].

Besides the functionalization of the external surface of molecular sieves, as described above, the internal surface of pure silica

MFI has been functionalized by post-synthesis surface treatments with methanol [144,145] or larger alcohols [146]. In the case of methanol it was suggested to be located in the zeolite structure bonded through $\equiv\text{Si}-\text{O}-\text{CH}_3$ linkages [147], and its presence had a limited effect on the properties of the host zeolite due to the small size of the methyl group. When functionalizing with 1-butanol and 1-hexanol, the characterization results confirmed the covalent bonding of these molecules almost exclusively to the internal silanol defect sites. Thus, using organic alcohols of different sizes will lead to hybrid materials with different pore properties [146].

4. Catalyst conformation for industrial use

As detailed by Bartholomew and Farrauto in [148], commercial heterogeneous catalysts are chemically and physically complex materials, and their development is a highly multidisciplinary task that requires inputs from chemistry, chemical engineering, material science and physics. In its final state, the catalyst has to accomplish specific dynamic properties which include: activity, selectivity, structure, surface composition or state of the active phase, and physical properties regarding its texture, density and mechanical stability.

A typical heterogeneous catalyst contains three components: an active catalytic phase, a promoter and a high surface area carrier or support. In the case of zeolitic catalysts the active phase can be the zeolite itself, and/or it can be used as a support for a second catalytic function.

Before forming the zeolite based catalyst it is necessary to synthesize, modify and activate the zeolite, and then combine it with the rest of the catalyst components. The next step in the catalyst manufacture involves shaping the components into microspheres, pellets or extrudates, among others. This can be the final process in catalyst manufacture, unless an additional catalytic function has to be later incorporated, for instance, by impregnation. The morphology of the final catalyst particle, i.e. size, shape, porosity, active site distribution, is determinant for the intrinsic reaction kinetics and for the diffusion rates of reactants and products, and it is generally marked by the type of reactor used [149]. Thus, fixed bed reactors require large particles (1–5 mm) in order to minimize the pressure drop along the reactor, and the particles must have a high

mechanical resistance. Pellets, rings and extrudates are commonly used here. In this case it is important to optimize the surface-over-volume ratio in order to minimize diffusional problems, and this can be done by varying the shape of the particles (cylinders, trilobes, hollow extrudates or rings, among others). Spheres (1–3 mm) are used for moving bed applications, and microspheres (40–100 μm) are the choice for fluidized bed or transported reactors. Having the adequate mechanical transport properties and attrition resistance is essential in all cases. Finally, monolithic catalysts are used in processes where it is crucial to maintain a low pressure drop while working with high flows of gases. Monoliths are continuous structures formed by parallel channels of 1–3 mm in diameter. The support is usually a ceramic or metallic material and is coated with a layer containing the active components. It is possible to vary the shape of the channels, and the monolith structure can be adapted to fit in the reaction chamber [149]. One of the most important applications based on monolithic catalysts is in the cleaning of automotive exhaust gases. More applications can be found in [149], and the importance of the final shaping step in large-scale use of zeolite based catalysts is also highlighted in [150].

5. Commercial processes based on inorganic molecular sieve catalysts

An interesting overview of the industrial relevance of zeolites and their use as heterogeneous catalysts, especially within refining and petrochemical processes, is given in [150]. Most of the zeolites used in catalytic processes are applied in this field, and other thorough revisions on this topic have also been published recently [2,25,32,151,152]. Here we will broaden the revision including applications in the field of chemicals and fine chemicals, in conversion of alternative energy sources such as natural gas or biomass, and in the treatment of emissions coming from stationary and mobile sources.

5.1. Oil refining

5.1.1. Fluid catalytic cracking

Fluid catalytic cracking (FCC) is the largest and oldest industrial application of zeolite based catalysts. The FCC unit is still a main conversion unit in many refineries, which is able to process very large amounts of heavy oil fractions. It is able to direct the production preferentially to gasoline, diesel (LCO), or it can maximize propylene, with minor modifications of the unit or in the operating conditions [153], thanks to the flexibility achieved with the FCC catalyst additives. The importance of zeolite based catalysts in FCC has been remarked in several recent revisions [2,152,154].

5.1.1.1. Zeolite based FCC catalysts. Zeolite Y replaced amorphous silica–alumina as the active component of FCC catalysts in the early 1960s, and has been successfully used since then. This zeolite, however, has been progressively improved in order to increase its activity and selectivity and to adapt the production to the desired products. Stabilization and ultra-stabilization of zeolite Y by introduction of rare-earths, dealumination by hydrothermal treatments combined with acid leaching, or combination of the two former procedures are well known procedures in the State of the Art. Phosphorus treatment of Y zeolite has also been claimed to increase its stability [155,156]. New zeolites with increasing pore size (>12MR), stable in FCC conditions, have been proposed for bottoms cracking. Some of them are ZSM-20 [157,158], or ITQ-21, with pore sizes in the range of those of the conventionally used Y zeolite but with a more open structure, which results in a higher olefinicity of the LPG obtained [57,159]. ITQ-33, with intersecting extra-large 18MR pores (12.2 Å) and 10MR channels [68], is an interesting zeolite able to increase simultaneously the yields to propylene and diesel,

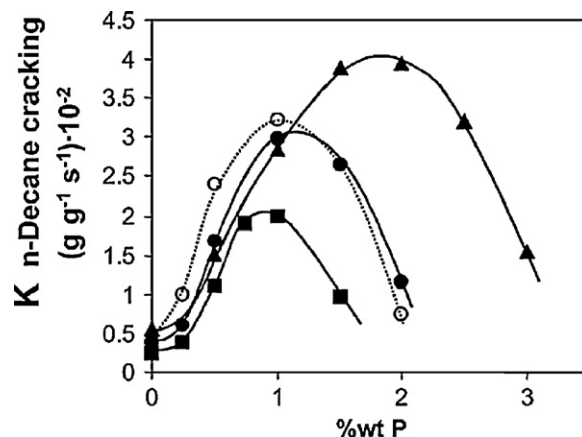


Fig. 10. First order kinetic rate constants in the cracking of n-decane of P-free and P-containing zeolite ZSM5 prepared by impregnation with H_3PO_4 and steamed at 750°C . (○) 25-ZM5-A, or with $\text{NH}_4\text{H}_2\text{PO}_4$ (▲) 15-ZSM5-P, (●) 25-ZSM5-P, (■) 40-ZSM5-P.

Taken from [160]. Reproduced with permission of Elsevier.

by a very peculiar molecular traffic control phenomena (Table 1). Unfortunately, the application of these new materials is limited in practice due to their still reduced hydrothermal stability and high production cost.

It should be remarked here that zeolites were introduced, instead of amorphous silica–alumina, mainly because their higher activity and selectivity to gasoline. However, the higher demand for diesel in several refineries in Europe may again chain the paradigm into more “amorphous” catalysts, i.e. catalysts containing more amorphous active matrix and less zeolite.

5.1.1.2. Zeolite based FCC additives. ZSM-5 containing additives are co-fed to the FCC unit in order to increase the yield of propylene and butenes, mostly at the cost of gasoline yield, but with a remarkable gain in gasoline octane. The medium pore ZSM-5 zeolite converts the linear and monobranched alkenes (as well as some alkanes) present in the gasoline fraction to light olefins, enriching the remaining gasoline in aromatics and isopentenenes. Hydrothermal stability of ZSM-5 is an important issue, and has been improved by modification with phosphorus, as shown in Fig. 10 [160–164].

Other medium pore zeolites studied as FCC additives are MCM-22 [165], ITQ-13 [61], IM-5 [166] and TNU-9 [167]. The increase in LPG yield and its olefinicity is in good agreement with their specific pore topologies and dimensions. Large pore zeolites such as Beta or ITQ-7 have also been proposed as FCC additives with the aim of increasing overall butenes [168], isobutane [14] or isobutene and amylene yields [169]. Although cost requirements are less stringent in the case of additives, the use of expensive organics or heteroatoms remain important drawbacks for commercial application of these new materials.

Besides the improvement of the FCC catalyst and additives, many efforts are directed to improve the design of the FCC unit, most of them regarding feed injection, stripper efficiency and catalyst recirculation. In all cases the trend is to adapt the units for processing different type of feeds and for flexible production, from distillate and fuel oils, to blend stocks for high octane gasoline or LPG and light olefins for petrochemicals and gasoline processes.

5.1.2. Hydrocracking

Hydrocracking is a highly versatile key process in modern refinery schemes, which enables the conversion of a wide variety of low-quality feedstocks such as atmospheric gas oils, vacuum gas oils, and heavier residues into lighter high-value added products, mainly transportation fuels. This permits the adjustments of product

Table 1

Catalytic cracking of Arabian light vacuum gasoil at 500 °C and 60 s time on-stream.

Catalyst	^a Conversion (%)	Yields (%)			Molar ratio	
		^b Diesel	^c Gasoline	C ₃ [−]	C ₃ [−] /C ₃	iC ₄ [−] /iC ₄
^d USY						
Cat/oil = 0.62	92.5	15.7	40.4	4.7	1.0	0.1
Cat/oil = 0.47	88.3	19.5	39.5	4.4	1.3	0.1
ITQ-33						
Cat/oil = 0.70	89.2	22.6	34.5	4.2	1.9	0.4
Beta						
Cat/oil = 0.70	84.0	14.1	32.3	7.5	1.9	0.5
USY + 20% ZSM-5						
Cat/oil = 0.47	87.0	17.0	33.2	7.2	1.5	0.3
ITQ-33 + 20% ZSM-5						
Cat/oil = 0.70	86.1	23.3	25.1	9.0	3.7	1.1

Adapted from [8].

^a The conversion is to diesel + gasoline + gases + coke.^b Diesel boiling point from 216.1 to −359.0 °C.^c Gasoline boiling point from 36.0 to −216.1 °C.^d Unit cell size of the USY zeolite is 2.432 nm.

specifications according to the new and stringent legislative requirements. In addition, during hydrocracking operation sulfur and nitrogen-containing compounds are removed and saturation of aromatics is also accomplished. The increasing diesel demand since year 2000, especially in Europe, has led to rebalance the refinery product distribution, and consequently, the long term desire would be to increase the number of hydrocracking units, especially for processing very heavy fractions, such as for instance Athabasca bitumen's or the very heavy products with high C/H ratios present in the Orinoco belt. Although hydrocracking units require large investments they can be a better option than thermal coking for processing very heavy crudes, as has been demonstrated by ENI with its Slurry Technology [170–174]. More details on the importance of zeolites as hydrocracking catalysts have been recently given by Rigutto [154], Perego and Carati [2] and Corma and Martínez [175].

Hydrocracking catalysts are bifunctional catalysts, comprising an acid and a hydrogenation–dehydrogenation function. According to their acid function they can be classified into zeolitic and non zeolitic catalysts. The non zeolitic catalysts are mainly formed by alumina and silica–alumina, and the zeolite based hydrocracking catalysts are grouped into low zeolite and high zeolite content catalysts. The zeolite is combined with amorphous silica–alumina in the first case, and with alumina, as binder and support, in the second case.

The zeolites used in hydrocracking conversion units are ultra-stable Y zeolites (USY), and their activity and selectivity to the different fractions (gases, naphtha, kerosene, diesel) will be determined by their acid properties, which are directly related to the framework (Si/Al) and extraframework Al content, and by their textural properties (micro and mesoporosity). These properties can be modified and adjusted through catalyst preparation. Regarding the hydrogenation–dehydrogenation function, it will be different according to the sulfur level of the feed. A noble metal, such as Pt, is used when processing low sulfur feeds as in the second stage hydrocracking unit. Transition metal sulfides are used for hydroconverting feeds with higher sulfur concentrations.

The zeolite-based hydrocracking catalysts are more active and more stable towards deactivation by coking or by basic nitrogen compounds than amorphous-based catalysts [176]. Their higher activity allows operating the unit at lower temperature, condition that favors aromatics hydrogenation, and therefore increases the quality of the middle distillates (higher cetane). On the other hand, they are less selective to middle distillates, as their conversion into naphtha and gases is favored on the stronger acid sites [177]. Therefore, and from the point of view of maximizing middle

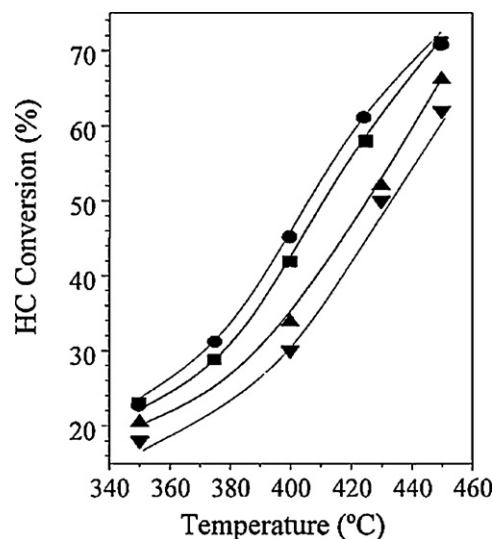


Fig. 11. Hydrocracking conversion obtained for the different catalysts as a function of reaction temperature at 3.0 MPa, 2 h^{−1} WHSV and 1000 H₂ (STP)/feed ratio. (●) NiMo/ITQ-2, (■) NiMo/USY, (▲) NiMo/ASA, (▼) NiMo/γ-Al₂O₃. Taken from [180]. Reproduced with permission of Elsevier.

distillates, it would be highly desirable to design hydrocracking catalysts that combine the good activity of the zeolite based catalysts with the high selectivity obtained with the amorphous silica–alumina. Thus, zeolite type materials with higher accessibility have been proposed in the literature, such as the very open zeolite ITQ-21 [178], nanocrystalline beta [179] or delaminated ITQ-2 [180] and clear benefits were obtained, not only from the selectivity but also from hydrocracking and hydrodesulfurization activity point of view (see Fig. 11 and Table 2).

Other large pore zeolites, such as ZSM-20 [181–183] or SAPO-37 [184,185] have also been claimed as hydrocracking catalysts. However, due to stability and economical factors, at present, zeolitic

Table 2

Selectivity of the different hydrocracked fractions obtained at ca. 55% hydrocracking conversion over NiMo-containing catalysts.

Catalyst	Gases	Naphtha	Middle distillates
NiMo/ITQ-2	14.1	34.3	51.6
NiMo/USY	18.9	34.1	51.6
NiMo/ASA	14.5	32.4	53.1

Adapted from [180].

commercial hydrocracking catalysts are based on zeolite Y. Modification of the zeolite's properties provides some flexibility according to the product distribution but, in the last years, there has been an increasing trend in using multi-component catalysts, where the acidic zeolite is combined with amorphous silica alumina (ASA) and an alumina binder. In this way, the alumina binder will enhance NiMo dispersion, the ASA will convert the larger molecules of the feed, and the zeolite will process the lighter fractions and the products obtained on the amorphous components of the catalyst [186,187]. Already in the early 1990s, John Ward (Union Oil) presented interesting results obtained when using combinations of Y with amorphous silica–magnesia as hydrocracking catalysts, and claimed the benefits in yields to middle distillates obtained by diluting the zeolite component [188].

Following a similar concept, a multizone hydrocracking process has been described where catalysts with different composition and/or shapes are placed in several consecutive reaction zones [189–194].

As in the case of FCC, the need for hydroprocessing heavier conventional feeds or unconventional crudes (tar sands, shale oils) require the improvement of existing technologies or the development of alternative strategies. The benefits of generating mesopores in Y zeolite as hydroprocessing catalyst have been largely described [130,131,195–197], and the combination of well-known procedures such as hydrothermal treatment–acid leaching with controlled desilication procedures has been proposed to be very advantageous (see the pore structures of the modified samples presented in Fig. 12), due to the improved diffusion properties of the final material [198]. Operation in reactors different from conventional fixed bed systems, such as ebullating beds or slurry reactors are alternative proposals [150].

Recently a new hydrocracking technology for heavy feeds has been presented by ENI that combines molybdenum nanoparticles and FCC equilibrium catalysts [170–174].

5.1.3. Catalytic dewaxing by cracking and alkane isomerization

Long chain n-paraffins are waxy compounds which can precipitate at low temperatures, providing lube oils and fuels with highly undesired cold properties (pour point, freezing point, cloud point). In the late 1960s and early 1970s catalytic dewaxing based on zeolites replaced the existing solvent dewaxing processes in the refining industry. These early zeolitic catalysts, in most cases medium pore molecular sieves, based their performance on their acid and shape selective properties. However, the first zeolite based bi-functional catalyst was proposed by BP, and involved a Pt/H-Mordenite [200]. Several years later, Mobil presented a ZSM-5 based catalyst [201], in where the lineal alkanes were selectively cracked with respect to branched ones. This is a clear example of reactant shape selectivity.

In the last decades a dewaxing process was introduced by Chevron (IsodewaxingTM) that combines selective hydrocracking with hydroisomerization, achieving in this way not only a reduction of the pour point, but also improved flow properties. A catalyst was proposed which contains SAPO-11 that favors isomerization, instead of cracking, of the waxy paraffins [202,203]. Exxon-Mobil has developed its Mobil Isomerization Dewaxing process (MIDW) based on a bifunctional noble metal-molecular sieve proprietary catalyst. According to Perego [204] the process involves two isomerization steps, one with a beta zeolite, and a second step with a monodimensional medium pore zeolite, such as ZSM-22. Different zeolitic structures have been compared for hydroisomerization of n-octane in [205] and the influence of the structure has been extrapolated to its potential behavior for dewaxing by isomerization. More details on the use of zeolites for dewaxing and dewaxing by isomerization can be found in [152,204,206].

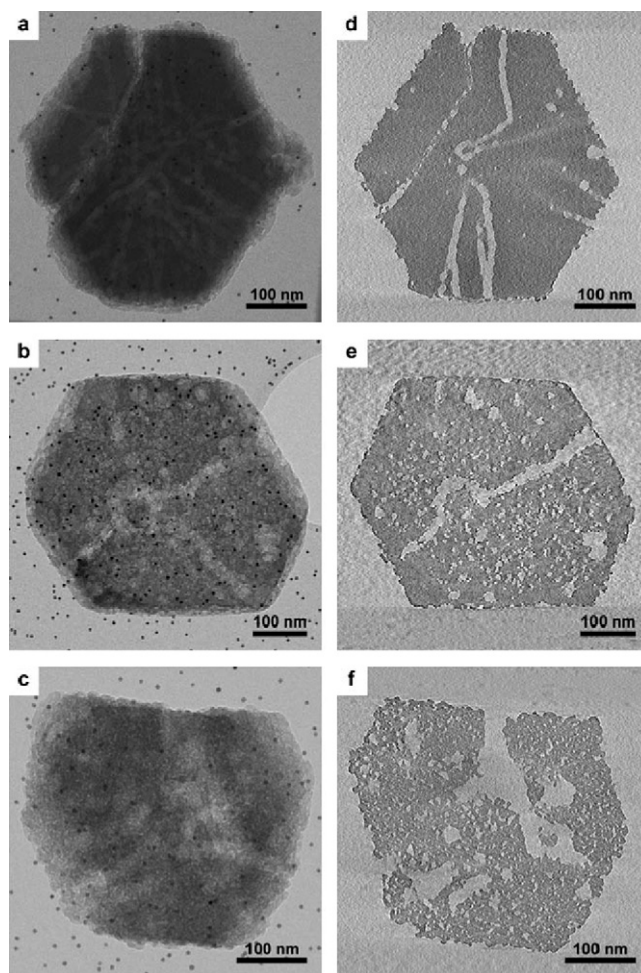


Fig. 12. Electron microscopy and electron tomography study of parent HY-30, base-leached HY-A (0.05 m NaOH) and HY-B (0.10 m NaOH) samples. The TEM micrographs show that base leaching of the parent HY-30 (a) leads to generation of more-porous structures as can be seen from HY-A (b) and HY-B (c), yet without revealing the true nature of the mesopore network. The numerical cross-sections through 3D reconstructions of the particles provided by electron tomography clearly depict the presence of both small (ca. 3 nm) and large (ca. 30 nm) mesopores, as well as their interconnectivity and shape: d) 0.56 nm thick slice of HY-30; e) 0.82 nm thick slice of HY-A; f) 0.56 nm thick slice of HY-B sample. Taken from [199]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

5.1.4. Production of aromatics

5.1.4.1. Non-oxidative conversion of methane to aromatics. Valorization of methane, the major component of natural gas, by its direct conversion into high value products, such as chemicals or fuels, is still one of the main challenges in heterogeneous catalysis. An attractive approach is the non-oxidative conversion of methane, which has been recently overviewed in several reviews and papers [207–212]. Despite the low conversions obtained due to thermodynamic limitations, the selectivity to benzene, the desired product, is high, and an effective separation of hydrogen during the reaction may shift the equilibrium towards the aromatic products.

The methane dehydroaromatization (MDA) was first presented by Wang et al. in 1993. The catalyst proposed for this process was a bifunctional Mo/H-ZSM-5, and the reaction was performed in the absence of oxygen at 700 °C and atmospheric pressure.

Mo, initially present as MoO₃, is converted during the reaction to a carbide-species and is involved in the dehydrogenation steps, while the zeolite acid sites catalyze cracking, oligomerization, and cyclization reactions. Although this concept of bifunctional

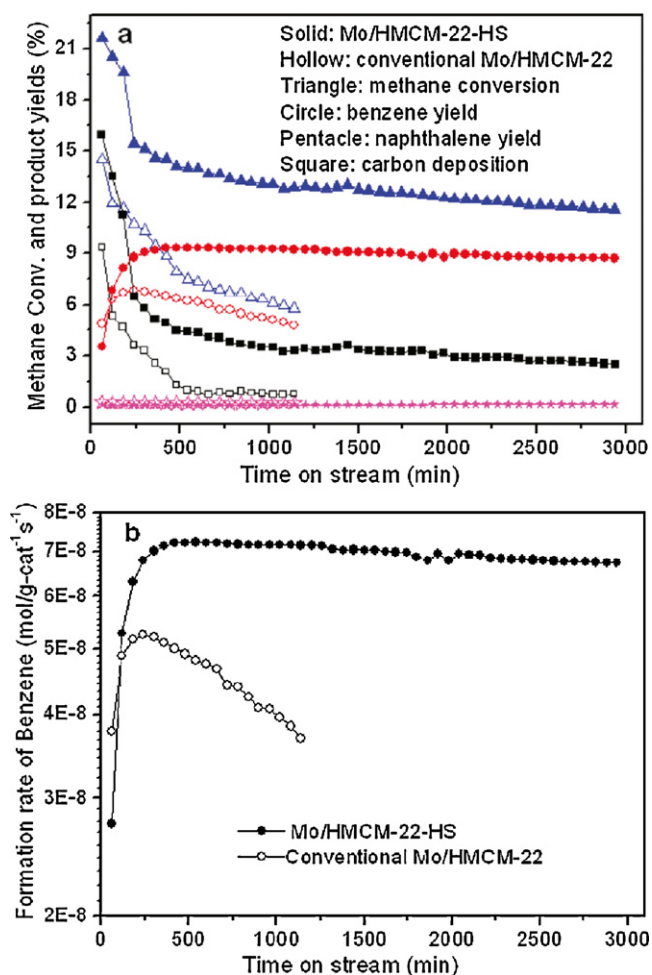


Fig. 13. (a) Catalytic performances of Mo/HMCM-22-HS and conventional Mo/HMCM-22 catalysts for MDA reaction; (b) formation rates of benzene at 973 K on these two catalysts under space velocity of 1500 mL/(g h). Taken from [215]. Reproduced with permission of ACS.

performance is generally accepted, details on the possible reaction mechanisms, as well as on the nature and role of the carbonaceous deposits formed during the course of the reaction are still not fully understood, and clear relationships between the nature of the catalyst and its performance have not yet been discovered. In all cases, an induction period is observed at the early stage of the reaction, probably related to the reduction of the MoOx species by methane into Mo-carbide and/or Mo-oxocarbide species. During this period only coke and gaseous products (CO , H_2O , H_2 and CO) are observed, with very little hydrocarbon formation. Thus, coking of the catalyst occurs during the reaction, leading to a severe activity loss, and this deactivation rate will be greatly influenced by the pore architecture and the acidity of the catalyst. Studies on the effect of the Si/Al ratio of ZSM-5 or ITQ-2 zeolites on activity and selectivity have been carried out by Martínez et al. in [213,214], respectively. It was found that rate of aromatics formation increased when decreasing Si/Al ratio, but maximum selectivity to benzene was obtained at intermediate values, and improved when dealuminating the external surface. Some recent papers present the superior performance of zeolites with hierarchical structures containing mesoporosity [215,216]. The benefits of these type of structures are a higher catalytic activity due to better Mo dispersion, a higher selectivity to benzene and a lower deactivation rate and increased catalyst lifetime, due to an easier and faster diffusion of larger molecules. This improved catalytic performance is illustrated in Fig. 13, where

activity and product yields for methane dehydroaromatization obtained with a conventional MCM-22 is compared with that given by nestlike hollow hierarchical MCM-22 microspheres [215].

The non-oxidative catalytic conversion of methane is usually carried out at 700 °C (or higher) applying plug-flow hydrodynamics in a continuous flow system under atmospheric pressure (or slightly higher) and in the absence of oxygen. The reaction is limited by thermodynamic equilibrium (maximum conversion of 12% at 700 °C). Increasing the temperature increases the formation of polyaromatics, coking and the difficulty of regeneration. The use membrane reactors has been proposed as a possible solution to overcome equilibrium limitations and application of measures to reduce deactivation.

5.1.4.2. Aromatization of short (C_2 – C_4) alkanes. The industrial conversion of short C_2 – C_4 alkanes (LPG) into aromatics, mainly benzene, toluene and xylenes (BTX), uses a zeolite based catalyst. The overall process can be described as a dehydrocyclodimerization, and is thermodynamically favored at temperatures above 425 °C. The rate determining step is the dehydrogenation of the light paraffins. The olefins formed are highly reactive and oligomerize to larger intermediates which then cyclize to naphthenes. Finally the naphthenes are dehydrogenated to aromatics. One additional advantage of this process is the generation of large amounts of H_2 , a high value by-product that can be further used in other refining or petrochemical units. One of the commercial aromatization processes is the Cyclar process developed jointly by BP and UOP, which employs a bifunctional Ga/HZSM-5 catalyst [217]. Typically, the optimum performance is obtained with catalysts containing 1–5 wt% Ga and Si/Al ratios in the range of 15–30, yielding about 65% aromatics and 5% hydrogen.

5.1.4.3. Catalytic reforming of naphtha. Although the former processes for aromatics production are gaining interest, most of the aromatics are obtained today by catalytic reforming of low octane n-alkanes and cycloalkanes present in the petroleum naphtha. Catalytic reforming process results in the production of high octane gasoline, hydrogen and BTX aromatics, and is present in almost 70% of all refineries [218]. For instance, the Aromax process, commercialized by Chevron, produces high yields of BTX from paraffinic naphthas (C_6 – C_8) by means of a Pt containing L zeolite [219]. At present, some reforming technologies are combined with other processes to upgrade the primary reforming products. For example benzene and toluene, whose concentrations are limited in the final gasoline pool, are alkylated with the olefins produced by cracking during the process. The benefit is double, as octane number and liquid yield increase, due to a lower gas production. Following this approach, Exxon-Mobil proposes the BTXtra process and the Benzene Reduction (MBR) process based on a ZSM-5 containing catalyst [220]. A deeper insight into catalytic reforming processes can be found in [152,204].

5.1.5. Isomerization processes

The isomerization process is equilibrium limited, and the formation of the branched isomers is thermodynamically favored at lower reaction temperatures. Thus, highly active catalysts are needed to achieve higher branching degree at lower temperatures, especially when converting n-alkanes. A large number of the current commercial processes use chlorinated $\text{Pt}/\text{Al}_2\text{O}_3$, a catalyst that requires the continuous addition of chlorine during the process. Nevertheless, an important number of units use a zeolite based bifunctional catalyst that avoids the use of chlorine derived additives and is more resistant to the presence of sulfur in the feed. Other strong solid acid catalysts such as modified zirconias and heteropolyacids have been sought with the aim of operating at lower temperatures than zeolites [221], but their implementation, if any, is very limited.

5.1.5.1. Isomerization of light straight run (LSR) naphtha. The isomerization of light naphtha fractions has gained importance in the last decades due to the new gasoline specifications, and the demand for isomerate as high octane blending component for the gasoline pool is expected to grow. Isomerate is an environmentally clean stream, free of aromatics, sulfur and olefins, and it can be obtained with relatively low investment costs. Moreover, the levels of benzene are significantly reduced in most of the isomerization processes.

Chlorinated alumina catalysts, although more active than the zeolite based catalysts, present the additional disadvantage of being highly sensitive to all kinds of feed contaminants, especially water and sulfur. Zeolitic catalysts are much more tolerant to these feedstock poisons, and this higher tolerance often compensates their lower activity. This was the basis for the development of Süd-Chemie's HYSOPAR[®] catalyst and the CKS ISOM process, jointly offered by CEPSCA, KBR and Süd-Chemie for light naphtha isomerization [222–224]. HYSOPAR is a platinum containing modified mordenite that can operate commercially at sulfur levels exceeding 50 ppm [225]. It was applied commercially for the first time in a light naphtha isomerization plant of CEPSCA's refinery in Algeciras (Spain) in 1993. Since then the catalyst has only been replaced twice, and actually more than 20 refineries around the world employ this robust catalyst. UOP commercializes several light naphtha isomerization technologies, the Penex[™] and the Par-Isom[™] processes, based on non-zeolitic catalysts, and their Zeolitic isomerization process, which uses a platinum containing mordenite catalyst.

5.1.5.2. Skeletal isomerization of linear butenes. Skeletal isomerization of light olefins to isobutylene and isoamylenes produces suitable feedstock for MTBE and TAME units or for the production of trimethylpentanes. The ISOMPLUS[™] process is a fixed bed skeletal olefin isomerization technology for converting n-butenes and n-pentenes to isobutylene and isoamylenes, respectively. In both cases a zeolite based catalyst is used [226] (Refining Processes 2006), which, according to Rossini [227], is a non modified ferrierite [228–230]. The feedstocks can be processed without steam or other diluents, and the addition of catalyst activation agents to promote the reaction is unnecessary.

Ferrierite, although modified, is also used as olefin skeletal isomerization catalyst in the Isotex process by Texaco [231–234]. Together with ferrierite, alumina modified materials are also used as catalysts in C4–C5 olefins oligomerization, as for instance in the SISP process by Snamprogetti [235,236].

5.1.6. Isobutane/butene alkylation

Alkylation processes are well known and widely used in the refining industry. In the case of isobutane/butene alkylation, the objective is to obtain high octane gasoline fractions [237,238], and the process is carried out in the presence of an acid catalyst.

The alkylate product is an ideal blending component for the gasoline pool, as it is sulfur, olefin and aromatic free, and contains exclusively high octane, low vapor pressure branched alkane compounds. Currently, industrial alkylation processes use liquid acids, i.e. HF and H₂SO₄, as catalysts [237,239,240]. In both cases the main problems are related to corrosion, transport and handling, and environmental risk related to the disposal of spent acid [241]. Undoubtedly, the substitution of these liquid acids by heterogeneous, environmentally more friendly solid acid catalysts is highly desirable. An updated review on homogeneous and heterogeneous alkylation chemistry and technology has been published recently [240].

Although processes based on solid acids are still not operated at industrial scale [240,242], several companies are developing processes or offering technology for licensing. Rapid deactivation

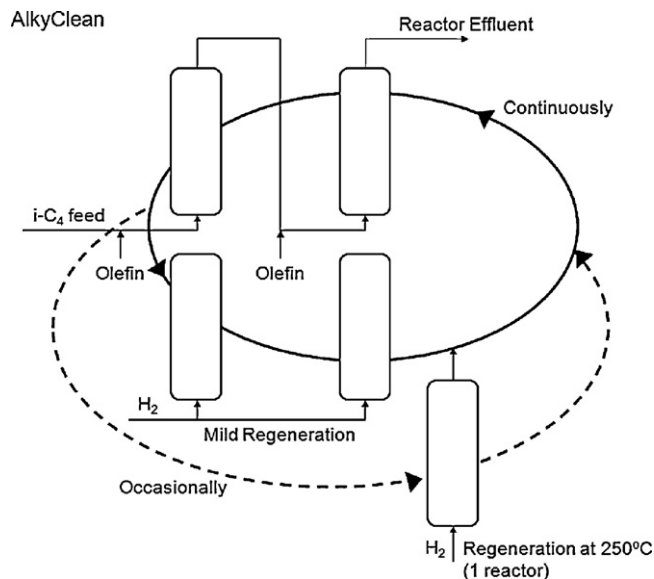


Fig. 14. Simplified scheme of AlkyClean process. Adapted from [255].

of the solid catalyst has been the main concern of heterogeneous alkylation processes during the last years, and the main challenge is to achieve adequate catalyst stability. In any case, solid acid catalysts have to be regenerated, and regeneration in the presence of hydrogen seems to be the preferred solution. At present, the solid acid alkylation technology developed seems to be able to compete with the existing homogeneous processes, and their commercial application in a near future will only depend on environmental issues [240]. Some of the zeolite using technologies available are the Exelus ExSact process, recently scaled up and proven in a pilot plant [242–249], or the ABB Lummus Alkylclean process schematized in Fig. 14 [250–252], whose catalyst is a noble metal containing zeolite with low sensitivity towards feedstock variation and common impurities [253,254]. The former is based on a novel fixed-bed reactor designed to enhance the performance of a solid-acid catalyst [242], wherein the fine-tuning of the micropores' diameter improves catalyst life-time by 40% by enhancing transport processes and reducing deactivation by coke formation and pore mouth plugging. Moreover, the optimum strength and distribution of the active sites enhances the product selectivity. The AlkyClean process uses cyclic multi-staged reactors operation (see Fig. 14), that alternates periods of on-line alkylation and mild catalyst regenerations (rejuvenation), allowing the plant to operate in a continuous mode maintaining the product quality. Intermittently one of the reactors is taken off-line for higher temperature H₂ regeneration.

5.1.7. Dimerization and oligomerization processes

Oligomerization of light olefins, such as propene and butenes, is an important industrial route for producing synthetic liquid fuels free of aromatics and sulfur. They are known to be flexible processes, able to produce olefinic mixtures, either in the range of gasoline or diesel. Modifying the catalyst and the operation conditions it is possible to obtain these two fractions with the desired characteristics regarding chain length and branching degree. Thus, high temperatures (>300 °C) and low pressures (≤30 bar) will favor the formation of oligomers in the gasoline fraction, whereas lower temperatures and higher pressures will increase the yield of heavier products in the diesel range. Concerning the catalyst, if based on acid zeolites, the reaction mechanism involves carbenium ions and, at least in the absence of steric constraints, the formation of

Table 3
MOGD product quality.

	Distillate	
	Raw	Hydrotreated
Specific gravity 15°/15°	0.79	0.78
Bromine no.	79	4.0
Aromatic, vol.%	–	3.0
Pour point, °C	<–50	<–50
Viscosity, cs at 40 °C	–	2.5
Cetane no. (engine)	33	56
Sulfur, wt.%	<0.002	<0.002
90% B.P., °C	333	343
Gasoline		
Specific gravity 15°/15°	0.73	
Octane	92	
R + O	92	
M + O	79	

Adapted from [260].

a highly branched product is favored. Thus, no shape selectivity is required for production of gasoline, as trimethylpentenes are the desired products. However, oligomerization of lower alkenes into high quality diesel is a complex task. Two different strategies have been proposed to face this problem: the first approach is the modification of the strength and environment of the acid centre, and the second one is the application of the well-known concept of “shape selectivity”. If zeolites with the adequate pore dimensions are used it will be possible to control the chain growth and the branching degree [227].

Medium pore zeolites are the most adequate for olefin oligomerization to high quality middle distillates. Large pore zeolites, such as HNaY [256] or Ni exchanged Y zeolite [257] have been described, but fast deactivation and low selectivity to long, straight-chain hydrocarbons desired for high quality diesel makes them not suitable for this process.

Although different 10MR structures are claimed for this process in the patent literature, most of the articles are based on studies using MFI. Shape selective oligomerization of C2–C5 olefins to gasoline blending stocks is known since the 70s, but it was some years later when researchers from Mobil and Chevron showed that, in addition to gasoline, this zeolite converts propylene also to heavier compounds in the range of fuel oils [258,259]. One year later Tabak et al. published a detailed description of the catalytic behavior of ZMS-5 in their MOGD process [260], and Table 3 shows the product quality obtained for distillate and gasoline fractions. Other oligomerization processes are offered by Sud-Chemie (COD Sud-Chemie oligomerization process) [222,261] and ExxonMobil (EMOGAS process) [262]. Both processes use a proprietary zeolite based catalyst.

5.2. Petrochemistry

5.2.1. Production of para-xylene

Para-xylene (PX) is the most valuable xylene isomer, and is used in the production of terephthalic acid (TPA) and dimethyl terephthalate (DMT), two intermediates in the manufacture of polyethylene terephthalate (PET) further used in polyester fibers, molded plastics, and films. The C₈ alkylaromatic mixtures obtained from reformat and from the pyrolysis gasoline, are the main sources of xylenes. In a first step the p-xylene present is separated from the C₈ aromatics mixture by selective adsorption on molecular sieves or by crystallization, and the remaining mixture is further upgraded to increase the yield of the desired para isomer by catalytic isomerization. Ethylbenzene is also present in these xylenes mixtures, its content may vary from 20 up to 50% according to the cut's source, and is difficult to separate from the xylenes

mixture. Thus, xylenes isomerization units have to deal with these high concentrations of EB that has to be converted. This is done by hydro-isomerization of EB to xylenes, a process thermodynamically limited, on a Pt-mordenite catalyst [263], or by hydro-dealkylation to benzene and ethylene with the medium pore ZSM-5 [150,152].

Xylenes isomerization is a well known process, which is performed with a ZSM-5 zeolite taking advantage of its shape selectivity properties and low coking tendency [204]. The combination of configurational diffusion and restricted transition state selectivity avoids the competing xylene disproportionation, reducing therefore xylene losses [264]. Fig. 15 illustrates the contribution of these disproportionation reactions for zeolite structures of different pore sizes, as well as the para-selectivity [265].

Considering ZSM-5, para-selectivity can be further improved by increasing the crystallite size or by selectivation of the external surface, which avoids unselective reactions to occur, but also by using zeolites with larger crystallites [266] and/or by eliminating the acid sites at the external surface through selective surface dealumination, chemical deposition of bulky organosilicon compounds, or coke-selectivation treatments [267–271].

Other possible processes for production of xylenes are transalkylation of toluene and C₉+ aromatics, or toluene alkylation with methanol. In the first case, the medium-pore zeolites are usually replaced by large-pore zeolites, preferably mordenite [272]. Catalyst life may be increased by the addition of a metal function.

In the case of toluene alkylation with methanol the catalysts used are ZSM-5, modified for increasing the selectivity to the desired p-isomer [273], La-modified MCM-22 [274], SAPO-11 or large pore mordenite or Y zeolite [275,276].

Finally, p-xylene can also be produced by disproportionation of toluene [277]. This bimolecular acid catalyzed reaction is carried out with medium pore zeolites such as ZSM-5 or MCM-22 [278,279], and also in this case selectivation of the zeolite surface has a beneficial effect [280], producing higher p-xylene yields together with the high valuable benzene.

Several commercial technologies for p-xylene production are detailed in [281]. The UOP Isomar and Parex processes are used to produce the desired p-isomer from the C₈-aromatics mixture, and the PX-plus XP process produces p-xylene and benzene by disproportionation of toluene. Exxon-Mobil Chemicals and Axens also offer technologies for p-xylene production by toluene disproportionation. The former process uses an in situ coke selectivated catalyst, increasing in this way the para-selectivity and the catalyst life. Axens has also an application for conversion of reformed naphtha into aromatics, the ParamaX process.

5.2.2. Alkylation of aromatics

5.2.2.1. Ethylbenzene production. Ethylbenzene (EB) is mainly used as intermediate for the production of styrene, an important monomer from an industrial point of view. Most of the processes synthesize EB from benzene and ethylene, and the worldwide capacity amounts to 20 million tonnes/year. Traditional processes which produced ethylbenzene from benzene and ethylene using Friedel-Crafts catalysts, e.g. AlCl₃–HCl, under mild conditions (160 °C) started operation in the 1930s. These processes, carried out in liquid phase, present important corrosion problems, and reactors were necessarily enameled or glass lined. To overcome these drawbacks supported catalysts were proposed in the 1960s, such as the SPA gas phase operation or the Alkar™ process from UOP, based on BF₃/Al₂O₃ liquid phase operation. However, corrosion was not totally avoided, the catalysts were not regenerable and were not active for transalkylation. Thus, better alternatives, such as true heterogeneous catalysts, were needed.

The Mobil/Badger process for gas phase ethylbenzene production in the presence of shape selective ZSM-5 zeolite was the first commercial zeolite based EB process. Its first plant, with 1 MMM

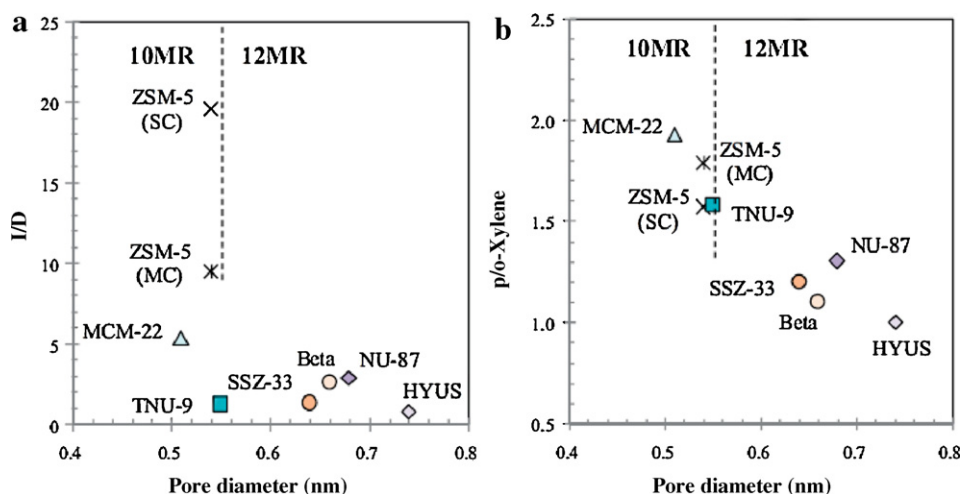


Fig. 15. Initial isomerization/disproportionation ratio (a) and para/ortho-xylene ratio (b) in m-xylene test obtained over different zeolites structures at 623 K and 10 s time-on-stream.

Taken from [265]. Reproduced with permission of Elsevier.

lb/year capacity, came on-stream in 1980. Since then, Mobil has been awarded 45 licenses [281] and the process accounts for 90% of all new EB-processes installed according to [30]. Currently Mobil Oil also licenses the Badger EB-Max technology based on a proprietary ExxonMobil alkylation and transalkylation catalyst [30,281], which is claimed to be a MCM-22 type zeolite, very stable and very selective to the monoalkylated product. This allows the process to use low benzene to ethylene feed ratios (from 3 to 5) and to reduce the benzene circulation rate [282].

Other ethylbenzene technologies are the liquid phase EB-One process licensed by ABB Lummus Global and UOP LLC, based on a proprietary modified Y zeolite catalyst from UOP, and the process developed by CDTech and based on catalytic distillation principles, also carried out in the presence of a zeolitic Y catalyst [30,281,282].

5.2.2.2. Cumene production. Cumene is an intermediate for phenol and acetone production, and the worldwide capacity of this process is around 8 million tonnes per year, distributed over around 40 plants.

The first industrial process used free sulfuric acid as catalyst, which was replaced in the late 1940s by a new technology based on solid phosphoric acid (SPA) developed by UOP. However, SPA presents a negative environmental impact, besides corrosion and handling problems. Thus, its substitution by environmentally more friendly solid acids, such as zeolites, was desirable. Initially the medium pore ZSM-5 zeolite, which was used in the Mobil-Badger ethylbenzene process, was studied as catalyst for gas phase cumene synthesis, but it was only when efforts moved into large pore zeolites and liquid phase operation, when results started to appear attractive from an applied point of view. The zeolites based processes produce higher cumene yields than conventional SPA process as most of the diisopropylbenzene byproduct is converted to cumene in separate transalkylation units. The absence of corrosion reduces operating and maintenance costs and zeolites can be easily regenerated and safely disposed.

The zeolites employed for the cumene production processes are generally large pore materials, which present no diffusional restrictions for cumene through the 12MR pores. The exception is MCM-22 (or MCM-56), a zeolite with medium pores and independent system of 12MR large cavities connected by 10MR windows, that presents an unexpected good catalytic behavior, comparable to that of a large pore zeolite. This has been explained by the complex porous channel system of MWW structure, formed, as described above, by two non-interconnected pore systems, both presenting

10 MR openings. One of them is formed by sinusoidal channels, with a slightly elliptical section, and the other is constituted by large supercages (18 Å long and 7.1 Å wide).

Perego et al. showed that the diffusion of cumene in the pores of MCM-22 was hampered by a high energy barrier [283]. Moreover, Sastre et al. [284] presented by means of molecular dynamic simulation that even benzene presented a low diffusivity in either of the two pore systems of the MWW structure, and cumene could not diffuse through the 10 member ring channel system. In a comparative study of zeolites Beta and MCM-22 it was shown that the alkylation of benzene on MCM-22 takes place mainly on the external surface, which in this material is perfectly structured and formed by $\sim 0.7 \text{ nm} \times 0.7 \text{ nm}$ cups.

On the basis of this conclusion, the delaminated ITQ-2 zeolite [20,98], which combines external surface areas in the order of $800 \text{ m}^2 \text{ g}^{-1}$ with strong Brønsted acid sites of zeolitic type, was studied as catalyst for ethylbenzene and cumene production, and was proven to be highly active for alkylation of aromatics with light olefins, with increased activity and catalyst life as compared to MCM-22 [285], as shown in Fig. 16.

Some of the commercial cumene processes based on large pore zeolites which are currently available are the 3-DDM cumene process (Dow–Kellogg) [286], the Mobil–Badger cumene process [287], the CDTech (ABB Lummus [281], the Q-max (UOP) [281], or the Eni Polimeri Europa cumene process [288,289].

5.3. Production of chemicals and fine chemicals

The great variety of pore topologies and pore dimensions together with the possibility to tailor their acid–base properties as well as their easy and repeated regeneration, make zeolites very attractive materials to be used as heterogeneous catalysts for synthesis of chemicals and fine chemicals [290,291].

Many studies can be found in the open literature where zeolites are described as catalysts for acid catalyzed Friedel–Crafts acylations, hydroxyalkylation of aromatic compounds, Diels–Alder reactions, acetalization of carbonyl compounds, Fischer glycosylation reactions and isomerization reactions (isomerization of α -pinene and α -pinene oxide). Several reviews have been published by Chunshan Song related to the use of acid zeolites as shape selective catalysts for the conversion of polycyclic hydrocarbons to specialty chemicals (e.g. synthesis of 4,4'-dialkylbiphenyl compounds, with substituents ranging from isopropyl to methyl groups on the bicyclic structure) [292–297].

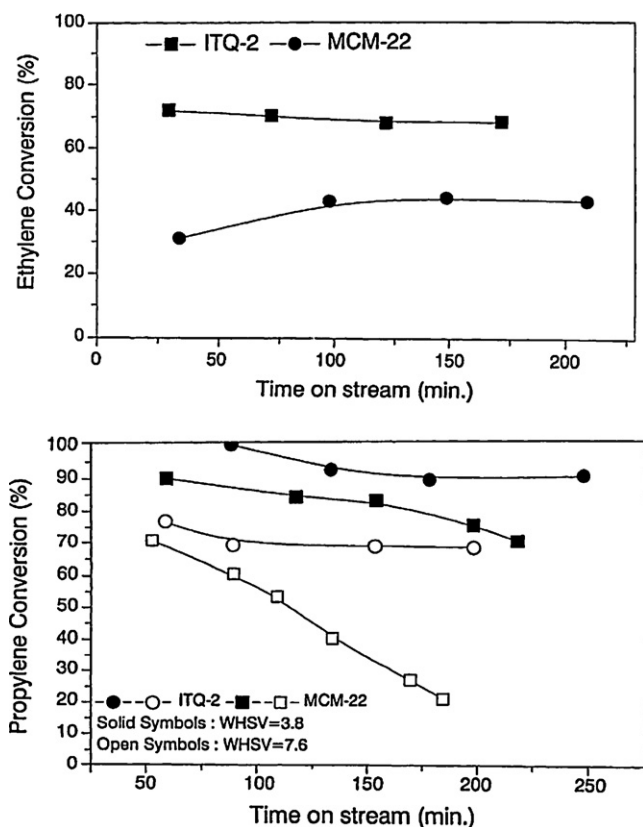


Fig. 16. MCM-22 and ITQ-2 as catalysts for alkylation of benzene (Bz) with ethylene (a), $P = 3.5$ MPa, $T = 240^\circ\text{C}$, Bz/olefin = 8 mol/mol, WHSV = 1.7 h^{-1} , and propylene (b) $P = 3.5$ MPa, $T = 220^\circ\text{C}$, Bz/olefin = 6 mol/mol, WHSV = 3.8 and 7.6 h^{-1} . Adapted from [285].

An important acid catalyzed process, which is still performed commercially with HCl, is the production of diamino diphenyl methane (DADPM), a key intermediate for the production of polyurethanes. The synthesis of DADPM, presented in Fig. 17, involves the condensation of two aniline molecules with one molecule of formaldehyde. Different solid acid catalysts have been proposed for this process, such as ion exchange resins [298,299], clays or amorphous silica–alumina [300]. Zeolites have also been

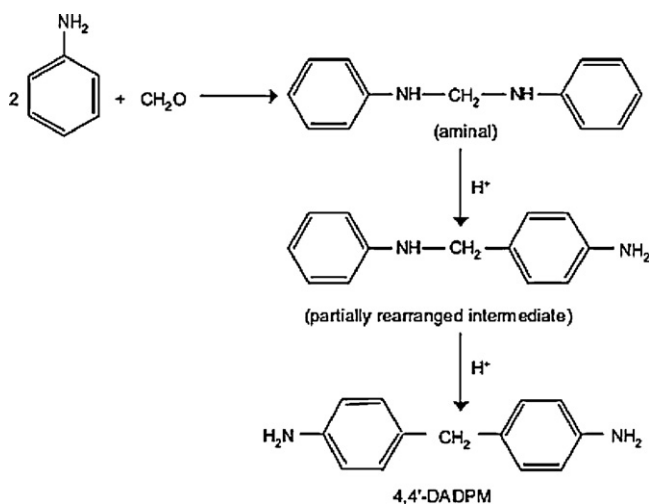


Fig. 17. Synthesis scheme of DADPM on solid acids. Taken from [305]. Reproduced by permission of The Royal Society of Chemistry; <http://dx.doi.org/10.1039/B406303A>.

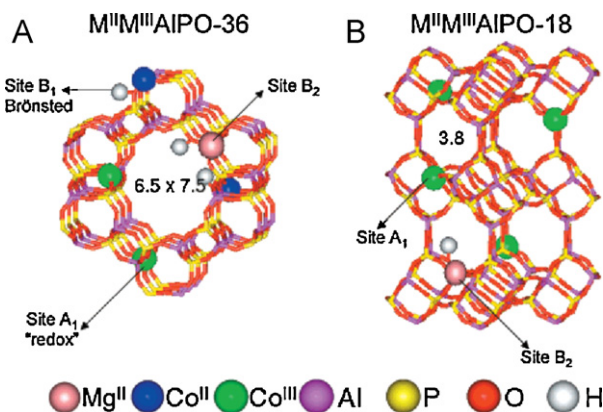


Fig. 18. (a) In $\text{M}^{\text{II}}\text{M}^{\text{III}}\text{ALPO-36}$ ($\text{M} = \text{Co}, \text{Mn}$), the framework M^{III} ions are the redox active centers (A1), whereas M^{II} ions have associated ionizable OH bonds attached to the framework and these are the Brønsted (B1) acid sites. Mg^{II} ions in the framework also have neighboring ionizable OH ions (B2 sites). (b) In $\text{M}^{\text{II}}\text{M}^{\text{III}}\text{ALPO-18}$ all the framework M^{III} ions are again redox active centers: there are no Co^{II} (or Mn^{II}) framework sites. Mg^{II} framework ions again have neighboring (B2) Brønsted sites. Taken from [310]. Reproduced with permission of ACS.

studied, and contribute with their characteristic shape selectivity, favoring the formation of the 4,4'-DADPM isomer. Y, ZSM-5 Beta, silylated Beta and ERB-1 zeolites have shown good catalytic properties [301–304]. They also present an additional advantage, their resistance to water. However, even very small crystal size beta zeolites present diffusional and deactivation problems. This has been very much improved by the use of delaminated zeolites, materials with a much higher accessibility to the active sites, which maintain the acidity, shape selectivity to 4,4'-DADPM and the water resistance of conventional zeolites. Their activity is higher than that of the nanocrystalline beta, and their deactivation rate is considerably slower [305].

The synthesis of ϵ -caprolactam, an intermediate for the production of Nylon-6 is currently performed in the presence of highly concentrated sulfuric acid, in a complex process with high environmental impact. An alternative route has been proposed where zeolite based catalysts, e.g. ZSM-5 and TS-1, are used in the different steps of the process, the hydration of cyclohexene to cyclohexanol and the oximation of cyclohexanone to cyclohexanone oxime [306,307].

Sumitomo chemicals has developed a new production process for caprolactam, by combining Sumitomo Chemical's proprietary catalysts with a new process from the Italian petrochemical company EniChem. The catalyst is a metal-containing pentasil-type zeolite structure and the process, environmentally friendly, does not generate ammonium sulfate [308,309].

An alternative route to ϵ -caprolactam is the direct ammoximation of cyclohexanone proposed by Thomas and Raja [310,311]. The final product is obtained by means of a one step solvent-free conversion of cyclohexanone to ϵ -caprolactam in the liquid phase using oxygen (air) and NH_3 . This reaction is catalyzed by structurally well defined ($\text{M}^{\text{II}}\text{M}^{\text{III}}$)ALPO-36 molecular sieve catalysts, where $\text{M} = \text{Co}, \text{Mn}$. The framework M^{III} ions are the redox active centers, whereas the OH bonds attached to the framework and associated to the divalent M^{II} ions are the Brønsted acid sites (see Fig. 18).

One of the most relevant applications of zeolites within the chemical industry is as a red-ox catalyst in propylene epoxidation. Other oxidation reactions studied on zeolitic materials are Baeyer–Villiger oxidations [312–316] or Meerwein–Ponndorf–Verley reduction [317] and Oppenauer oxidation (MPVO) [318].

An interesting chemical process is the methanol carbonylation for production of acetic acid, which is commercially performed by means of an homogeneous iridium/iodide based catalyst [320]. In

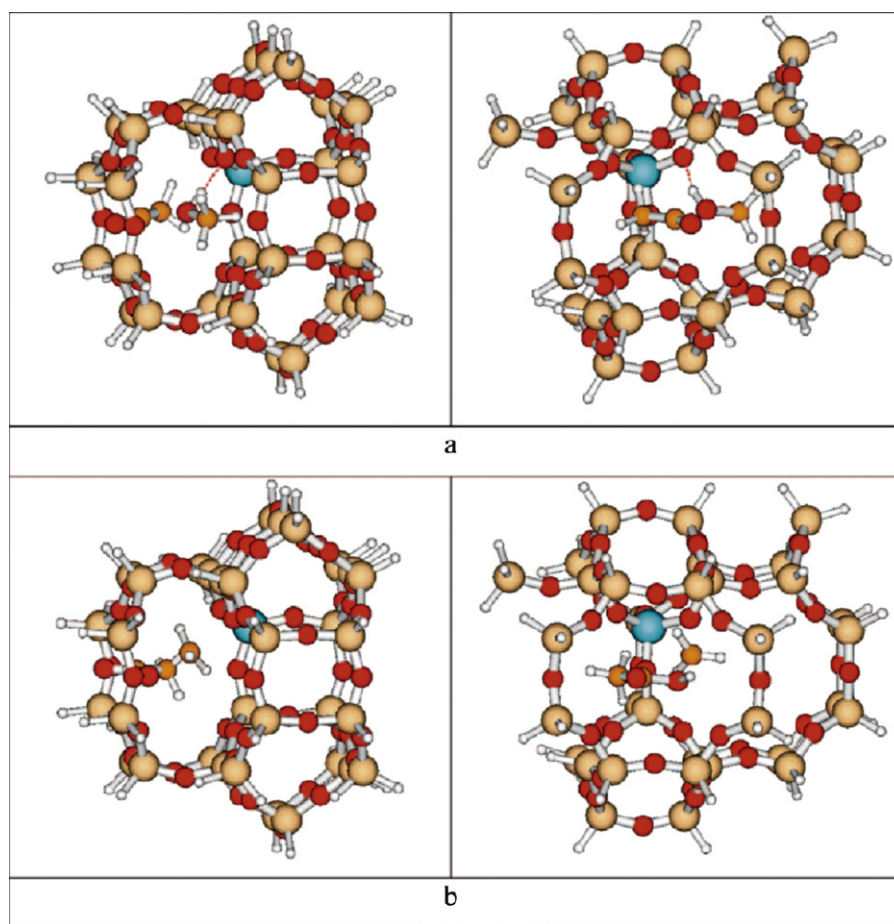


Fig. 19. (left) Side views and (right) face views of the optimized structures of the two different transition states obtained for the reaction of methanol with the acylium cation intermediate formed at the T3-O33 position in MOR: (a) reaction products are methyl acetate and a Brønsted acid site; (b) reaction products are acetic acid and a methoxy group.

Taken from [319]. Reproduced with permission of ACS.

the last years it has been shown that zeolites are able to catalyze the carbonylation of methanol or dimethyl ether (DME) with CO, in the practical absence of H₂O, with a high selectivity to methyl acetate [321–327]. Different zeolite structures have been tested as catalysts for the carbonylation of methanol, with mordenite being the most active and selective, followed by ferrierite. Both zeolite structures present 8-membered rings (8MR), and the reaction of methoxy groups with CO has been suggested to selectively occur within these 8MR pockets shown in Fig. 19 [323], whereas the acid sites present at the 12MR channels would favor the formation of hydrocarbons when working at higher temperatures. More details on the contribution of the different sites to the overall carbonylation reaction are given in [319].

Large pore zeolites have been proposed for isomerization of α -pinene oxide to campholenic aldehyde, and important intermediate for the synthesis of certain fragrances. The highly dispersed Lewis acid Al sites in a USY zeolite seem to be responsible for the good performance of this catalyst [328]. High selectivity to the desired products was obtained on Ti-beta, both in liquid and gas phase [329].

Finally, zeolites in their basic form have also been described as active for different C–C bond formation reactions, such as Knoevenagel condensation, Michael Additions and Aldol condensations, and for side-chain alkylation of aromatics. Most of these processes are commercially manufactured using homogeneous bases. One example of basic zeolite based process is the synthesis of 4-methyl-thiazole (4-MT) using Cs₂SO₄/ZSM-5 claimed by Merck & Co. researchers [31,330]. Although this process, as far as we know,

has not yet been commercialized, it reached the pilot plant stage in 2001 according to [29]. 4-MT is used in the production of thiobenzodazole, a systematic fungicide used for spoilage control of citrus fruit and for preventing Dutch elm disease in trees and fungal disease in seed potatoes [331], and can be synthesized in one single reaction step from acetone imine and SO₂ over a basic zeolite. In the presence of Cs-doped ZSM-5 (2 wt% Cs) this cyclization reaction occurs at 470 °C yielding 70% of 4-MT.

A revision of the current commercial applications of zeolites in fine chemicals can be found in [332]. Some of the processes highlighted there are the synthesis of ϵ -caprolactam, the synthesis of trioxane, the isomerization of α -pinene oxide, the synthesis of p-methoxyacetophenone, the production of 4-methylthiazole and the production of methyl methacrylate.

Zeolites and, in general, structured molecular sieves, still offer the scarcely explored possibility of multisite catalysts for selectively performing one-pot or cascade reactions, leading in this way to process intensification [333,334].

5.4. Emerging applications in energy and environment

5.4.1. Zeolites as catalyst for natural gas conversion

Natural gas appears as an attractive alternative source for fuels and chemicals, due to its abundance in natural reservoirs, its high H/C ratio and low undesired heteroatoms content. There are two main routes for natural gas (methane) valorization, the single step conversion of methane through direct routes, or the indirect routes, where methane is converted to the more reactive synthesis gas

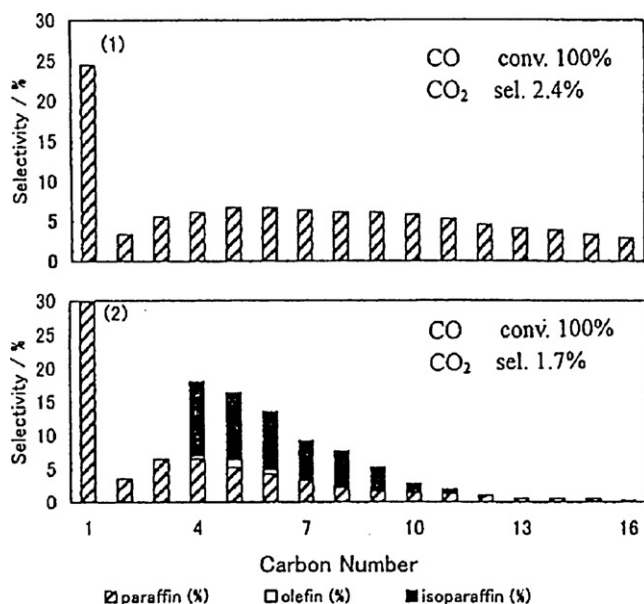


Fig. 20. Product distribution comparison of FTS reaction on hybrid catalyst and FTS catalysts. (1) Co/SiO₂, (2) Co/SiO₂ + ZSM-5. 513 K, 1.0 MPa, H₂/CO = 3, W(Co/SiO₂)/F = 11.5 g h/mol, total catalyst weight = 1 g. Taken from [337]. Reproduced with permission of Elsevier.

mixture, CO + H₂, in a previous process. The main direct routes are methane dehydroaromatization (MDA) and the nonoxidative coupling of methane (NOCM), both of them very unfavorable from the thermodynamic point of view. The low equilibrium conversions may be improved by selective extraction of H₂, one of the main products [335]. Mo-containing zeolites, mainly ZSM-5 but also MCM-22, have been thoroughly studied as catalysts for MDA [207,212]. This topic has already been covered in Section 5.1 as one of the processes for producing aromatics.

Processing of syngas offers many possibilities and a larger flexibility towards the final products. Fischer-Tropsch Synthesis (FTS) is a well-known process for syngas conversion in to synthetic liquid fuels. Moreover, the diesel fraction obtained in this way, formed mainly by linear paraffins, has an outstanding quality, with cetane numbers above 70, and very low contents of sulfur or polyaromatics. Conventional FTS catalysts are usually iron or cobalt promoted porous inorganic oxides, such as SiO₂, Al₂O₃ and TiO₂, and more details can be found in [336]. Ordered mesoporous silicas and delaminated zeolites (ITQ-2, ITQ-6) in their pure silica form have also been described as supports for Co based FT catalysts. The incorporation of the metal promoter is a key factor in the final catalytic behavior, and deposition of cobalt nanoparticles synthesized in the core of reverse micelles on previously silylated ITQ-2 has shown important benefits [335]. However, non-delaminated zeolites are less adequate than periodic mesoporous silicas as supports for conventional Co based FT catalysts for synthesis of long chain hydrocarbons or waxes, due to the limited dimensions of their pores. Moreover, acidity has to be avoided in this case.

Application of zeolites in syngas conversion has been contemplated for the so called modified FTS, which uses a hybrid or composite catalyst, formed usually by a mechanical mixture of a conventional iron or cobalt based FTS catalyst and a solid acid, such as for instance a zeolite. The objective of the zeolite component is to increase the yield and quality of liquid fuels, especially gasoline, by converting in situ the primary FTS hydrocarbons (α -olefins and long-chain n-paraffins) through cracking and isomerization reactions in a single stage process [335,337–339]. Beta, ZSM-5, MCM-22 and delaminated ITQ-2 are some of the structures proposed. Fig. 20 shows the increased selectivity to isoparaffins when

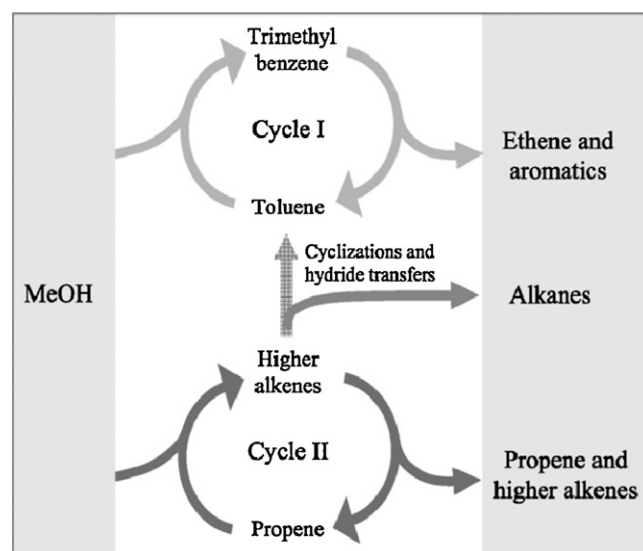


Fig. 21. Suggested dual cycle concept for the conversion of methanol over H-ZSM-5. Taken from [344]. Reproduced with permission of Elsevier.

combining FTS catalysts with ZSM-5. A detailed description of the application of zeolites in FT processes is given by Martínez and Prieto in [340].

5.4.2. Methanol to olefins (MTO) and methanol to gasoline (MTG)

Methanol is produced from synthesis gas which, in turn, is obtained by natural gas or coal reforming or even by gasification of lignocellulosic biomass. Although it could be used potentially as a fuel, alone or blended with gasoline, this would involve technical problems difficult to overcome. However, the conversion of methanol into olefins, highly valuable components within the petrochemical industry, or into high-quality gasoline, are two interesting alternative processes [341]. The MTO process is ready for commercialization, and UOP has already announced their SAPO-34 based process for ethylene production. The MTG process has been proven commercially, and the first MTG plant was constructed in New Zealand in 1979 [342]. However, due to the relative prices of methanol and gasoline, the plant currently only produces methanol. The catalysts are based on ZSM-5 and SAPO-34, and more details can be found in [342–346]. Fig. 21 shows a schematic representation of the dual cycle concept for the conversion of methanol over H-ZSM-5 suggested in [344].

5.4.3. Sustainable energy applications

Catalytic production of high quality biodiesel is a topic of increasing interest [347]. Some of the advantages of biodiesel as compared to other fuels are: the non-contribution to the net CO₂ concentration when combusted, the absence of sulfur and its biodegradability. As counterpart, for converting biomass into automotive fuels, a cheap and abundant biomass feedstock is needed, and the high oxygen content of this alternative fuel source has to be considered. Vegetable oils are triglyceride esters of fatty acids that need to be converted to a mixture of fatty acid methyl esters (FAME). Zeolites and mesoporous materials have been proposed to carry out this process selectively. However, biomass conversion involves the transformation of large and bulky molecules, which will not be able to access the zeolite micropores. Thus, the role of zeolites in the direct catalytic conversion of biomass is questionable [28], though they can be of interest for processing platform chemicals obtained from biomass (ethanol, furfural, glycerol, levulinic acid) [348–350].

Nevertheless, Perego and Bosetti [351] have recently presented a route for hydroprocessing of triglycerides with a bifunctional catalyst, the ECOFINING Technology jointly developed by ENI and UOP. This process uses a catalytic hydroprocessing/isomerization technology for conversion of vegetable oils or animal greases into a highly stable green diesel fuel, which is claimed to have better properties than biodiesel [352].

A biomass pyrolysis process has been presented recently for direct conversion of cellulosic biomass into liquid fuels in a single step by catalytic pyrolysis [353,354]. The catalyst is based on ZSM-5 zeolite, and the final product is a mixture of benzene, toluene and xylenes. At present, the process has only been demonstrated at a small scale.

5.4.4. Environmental applications

Environmental concern and development of catalytic processes for environment protection started in the 1990s, and since then a large number of technologies have been set forth. Centi and Perathoner have given a very complete overview for the different applications of zeolites as environmental catalysts [355]. We have seen in previous chapters that the substitution of less friendly homogenous catalysts by zeolite based solid catalysts results in environmentally compatible technologies and sustainable production processes. The same can be stated for the use of renewables and conversion of biomass. Here we will focus on catalytic clean-up technologies for emissions coming from stationary sources and for emissions from mobile sources (vehicle emissions). More specifically, the conversion of nitrogen oxides together with the elimination of VOCs from gas emissions are interesting fields for zeolite based catalysts.

High temperature combustion of fossil fuels and biomass produces nitrogen oxides (NO_x), which are responsible for acid rain and for the presence of ozone in the troposphere. Thus, their concentration in gaseous emissions from stationary sources, e.g. thermal power plants, gas turbines and incinerators is limited.

Concerning the emissions from mobile sources, the main problem is related to diesel engines. Their CO emission is lower than that of gasoline engines, the particle emission is solved by including a particle filter, but NO_x emissions should be avoided. The current Euro V emission standards for passenger cars, applied since 2009, limits the NO_x emissions in diesel to 0.18 g/km, and to 0.06 g/km in the case of gasoline. The level in the case of diesel will have to be decreased to 0.08 g/km by 2014. Thus, catalytic technologies for these exhaust gas treatments are facing an important challenge in this field.

An overall revision of the state of the art on catalytic removal of NO_x under lean conditions is given by Forzatti et al. in [356]. Currently the urea-ammonia selective catalytic reduction (SCR) technology is well established and is largely employed for NO_x control in stationary sources emissions, but commercial catalysts consist of homogeneous mixtures of tungsten and vanadium oxides (or molybdenum oxide) supported on high surface area titania in its anatase form, in the shape of honeycomb monoliths or plates to overcome pressure drop problems. Up to now, commercial application of zeolites for NO_x removal is still limited to adsorption processes. However, SCR using zeolite based catalysts is a viable option for reduction of NO_x from diesel engines using urea as reductant [357], and Cu/MFI and Fe/MFI, together with 8MR zeolites seem to be close to their commercial use for the control of diesel engine exhaust emissions, according to [355].

When considering zeolitic catalysts for NO_x SCR, the metals that seem most adequate are copper, cobalt and iron. Concerning the zeolite type, different structures have been described in the literature. Cu-ZSM-5 has been recognized for many years as a unique catalyst for direct NO conversion [358]. Other zeolites claimed were ZSM-11 or ZSM-12 [359,360]. However, recent in situ EPR

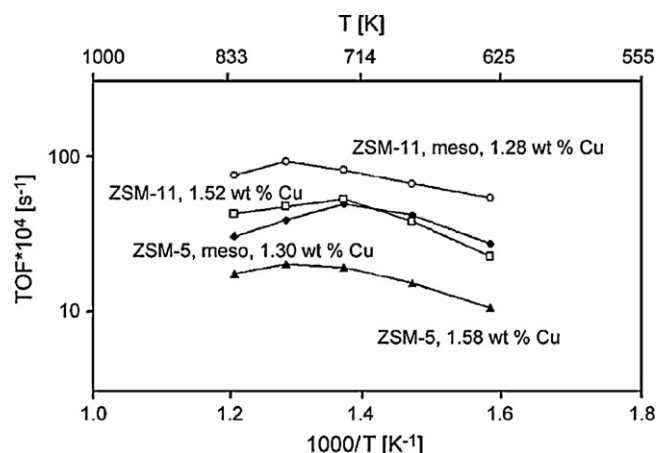


Fig. 22. Arrhenius plot illustrating the activity difference between conventional Cu-ZSM-5, Cu-ZSM-11 and mesoporous Cu-ZSM-5, Cu-ZSM-11 catalysts. The inlet concentration of NO was 1% NO in Ar. The total pressure was 1 atm. Taken from [362]. Reproduced with permission of Elsevier.

studies relate the higher activity of Cu-zeolites with an improved accessibility of the active sites, rather than to the structure itself, and shows a much higher activity on Cu-ZSM-11 and Cu-ZSM-12 than on Cu-ZSM-5. The advantage of ZSM-11 appears to be the fact that it only contains straight 10MR pores, whereas ZSM-5 has both straight and sinusoidal channels. Thus, in disagreement with previous observations, the special pore structure of Cu-ZSM-5 is not determinant for catalytic activity in NO decomposition [361]. Moreover, generation of mesoporosity in Cu-ZSM-5 and ZSM-11 significantly improves the catalytic behavior, and again Cu-ZSM-11 performs better than Cu-ZSM-5 [362] (see Fig. 22).

More important than the zeolite structure itself, the key issue for a good performing zeolite based SCR catalyst is the accessibility and nature of the active metal ion sites, and this will be influenced by the zeolite's Si/Al ratio and the preparation conditions. Due to the small size of the molecules involved in the process, shape selectivity effects or electrostatic stabilization inside the zeolite structure will not be significant.

Other zeolites studied are beta, IM-5 or ITQ-7. An XPS and XAES study of Cu-Beta with different Cu loadings, coupled with an in situ type of catalytic experiments conducted in a high-pressure gas cell installed in the preparation chamber of the spectrometer, showed that the most active Cu-Beta zeolites for SCR of NO_x were those in which a rapid conversion between Cu^{II} and Cu^I species occurred under reaction conditions, a conversion that was easier on over-exchanged Cu-Beta samples. The authors found a good correlation between the ratio of Cu^I to total Cu on the catalyst surface and catalytic activity [363]. ITQ-7, with a topology similar to that of zeolite beta, gave similar results when exchanged with Cu or Co [364]. Finally, Cu-IM5 has been described as more active and more stable hydrothermally than Cu-ZSM5 [365].

Very interesting results obtained with a physical mixture of tin dioxide and the acid zeolite and a second metal such as manganese or copper, as compared to tin-beta where the metal was introduced in the framework by synthesis or by ion exchange, suggest that the physical mixtures of metals with zeolites could be an interesting and inexpensive way to prepare active catalysts for this reaction [366]. Besides the high conversion for the NO_x removal of this catalytic system, it is not deactivated by water at lean burn conditions when the second metal is manganese, as shown in Fig. 23.

Researchers from Johnson Matthey Inc. presented a recent surface adsorption FTIR spectroscopy study on the differences in transient response and the effect of NO:NO₂ ratio on Fe or Cu exchanged zeolites in the SCR of NO_x with urea [367]. Still, the

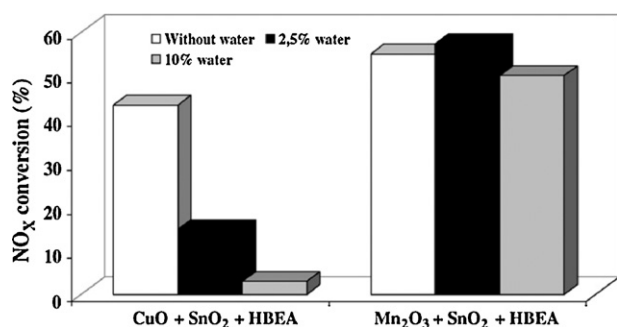


Fig. 23. Influence of the presence of water in the SCR of NO with propane at 623 K over H-Si/Al beta zeolite + SnO₂ + Mn₂O₃ (0.3:0.2:0.5, w/w/w) and H-Si/Al beta zeolite + SnO₂ + CuO (0.3:0.2:0.5, w/w/w), 730 ppm NO, 385 ppm C₃H₈, 14.5% oxygen, N₂ as effluent.

Taken from [366]. Reproduced with permission of Elsevier.

main drawback concerning the industrial use of zeolite based SCR catalyst is their long term hydrothermal stability [368–371]. Thus, the trend is to use small 8MR pore zeolites, much more stable in the highly demanding process conditions. Thus, copper promoted SSZ-13 and SAPO-34 (CHA structure) are some of the zeolites claimed in the recent patent literature by BASF or PQ Corp for selective reduction of NO_x.

6. Future perspectives in commercial application of inorganic molecular sieves as catalysts

The need to replace the currently remaining homogeneously catalyzed commercial processes by heterogeneous alternatives, and to improve existing technologies, offers to new molecular sieves and modified existing ones the possibility to be commercially applied. The use of high-throughput methodologies has already proven to be highly efficient, not only in the discovery of new materials, but also for synthesis optimization to improve the characteristics of already existing zeolite structures, from the point of view of the catalytic properties, as well as for reducing the synthesis costs by employing less expensive SDAs or by completely avoiding their use.

In the fields of refining and petrochemistry the industrial zeolite based processes are well established, but catalyst improvements for higher selectivity or catalyst life time will have an important economic impact. On the other hand, for the production of chemicals and fine chemicals, the application of zeolites will have to face important challenges, especially in the case of base catalyzed processes. The discovery of new materials, the synthesis of known zeolite structures by means of alternative, less expensive, synthesis routes (OSDA free), and their modification to generate nanocrystals, mesopores or composites of different zeolites, will play a decisive role for production of chemicals and fine chemicals.

The conversion of alternative raw materials is a rather new research line, and the use of zeolite based catalysts appears as a very attractive option. Indeed, for biomass transformations, zeolites can work in water media and their polarity (hydrophobicity–hydrophilicity) can be modulated. Furthermore, a very active research field in zeolites with high potential is related with the reduction of nitrogen oxides by selective catalytic reduction, especially when focused on small pore, highly hydrothermally stable zeolites.

7. Conclusions

More than 80% of all industrial processes are catalytic processes, and many of them use zeolite based catalysts. The number of industrial processes based on heterogeneous catalysts is increasing, not only in refining and petrochemical areas, but also in new emerging

fields. Some of the processes are well established, such as catalytic cracking and hydrocracking, light paraffins isomerization or aromatic alkylation. They require relatively inexpensive zeolites and probably only new zeolites with low cost production may have an opportunity. This is not necessarily the case for production of some chemicals and certainly not for fine chemicals, in where the impact of the catalyst cost on the final product is relatively low. The same could be said for the application of zeolites to automotive uses and for converting biomass derived products into higher value chemicals. Finally, we believe there may be new opportunities for zeolites with more than one type of pore in the same structure. Furthermore, one of the holy grails in the field of zeolites still is the synthesis of tridimensional extra-large pore hydrothermally stable zeolites. These materials may offer new possibilities for processes in chemicals, fine chemicals and biomass transformations. Meanwhile, for shape selectivity purposes, medium pore zeolites (especially uni- and bidimensional) will probably continue to play the most important role.

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