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PERSPECTIVE REVIEW

Zeolite science and technology at Eni

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In the last forty years Eni laboratories have contributed to the advancement of zeolite science and technology in both the materials synthesis and characterization and the application in catalysis. This work has led to several industrial applications for selective oxidations and acid-base catalysis as well as for gas separation and water remediation. A brief review of the main results is reported with some comments of the future perspectives for these branches of technology.

Introduction

Zeolites constitute an important and fascinating class of crystalline microporous materials, whose technological relevance is demonstrated by the extensive application as heterogeneous catalysts in several petrochemical and oil refining processes, as ion-exchangers for domestic and industrial uses, as molecular sieves for the separations of specific molecules from complex mixtures. As the major oil companies in the world, from the very beginning of the modern era of the science and technology of zeolites, Eni has recognized the potential provided by these materials investing significant resources in the preparation of new materials and in their applications, mainly (but not exclusively) in some of those fields which are traditionally its main businesses: petrochemistry and oil refining. Even within the limits imposed by being an industrial company, the research is conducted in a very open manner, giving due importance to the sharing of the results with the international scientific community. In fact, there is a strong belief that innovation can only benefit from the exchange of experiences and from the collaboration with leading research groups in the field. This allowed us to reach significant achievements, many of which remain of purely scientific interest and have been shared with the scientific community through several publications on international peer-reviewed journals, contributions to national and international conferences, invited lectures in universities and public/private research centres. On the other hand, some of them have been the basis for in the development of new industrial processes still used today in Eni's industrial sites or licensed to other companies in the world.

This paper is part of a special issue dedicated to Francois Fajula, a world-renowned scientist who has contributed in a decisive way to the advancement in the field of zeolites and related materials. It is superfluous to say that the experience and teaching received from scientists as Francois Fajula is very valuable for our daily research work and, therefore, we want to give him a sign of gratitude and esteem.

Here, we try to connect research on different chemical reactions and zeolite catalysis by a not so thin common thread. We will make a journey through the long research activity, with brief stops to describe the main achievements that, we do hope, demonstrate our contribution to the development of the science and technology of zeolites and related microporous materials.

Zeolite synthesis evolution at Eni

The progress in the petrochemical and oil refining industries is highly dependent on the technological innovation of the transformation processes that, in turn, require innovative materials with characteristics and properties tailored to the specific needs. Already at the dawn of the modern era of the science and technology of zeolites, Eni has recognized the high potential of the crystalline microporous materials, devoting considerable efforts and resources in research aimed at the preparation of new materials with innovative properties.

The guideline that has characterized research on zeolites at Eni in the last 40 years was to consider as new materials not only those characterized by a new structure, but also those resulting from the compositional and morphological modification of known phases. In this regard, considerable efforts have been devoted to the process known as "isomorphous substitution", consisting in the, at least partial, replacement of Al and/or Si with other tri- or tetravalent elements, capable of imparting new properties to the zeolite framework. In this way, the successful incorporation of Ti into the Silicalite-1 (MFI) framework, claimed by Taramasso *et al.*,[1] led to the discovery of Titanium-Silicalite-1 (TS-1), the first crystalline microporous

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oxidation catalyst particularly active and selective in oxidation reactions with H_2O_2 under mild conditions. The original recipe is based on the controlled hydrolysis of aqueous solutions containing tetraethyl orthosilicate, tetraethyl orthotitanate and tetrapropylammonium hydroxide. This mixed alkoxide procedure allows a fine control of the synthesis, favouring the crystallization of high quality TS-1 samples. [1] Once recognized the excellent properties of this catalyst, several alternative synthesis methods have been reported, but many of them lead to the crystallization of TS-1 samples of lower quality respect to the original material. [2] More recently, an improved synthetic method, operating at a particularly low dilution, has been developed. [3] With suitable H_2O/Ti molar ratios in the reaction mixture, TS-1 is prepared, in pure phase, with a high productivity. An extensive physico-chemical characterization of TS-1 allowed to assess that up to a maximum of 2.5 atom% of Ti are incorporated in the framework in tetrahedral coordination (Fig. 1) [2,4-9] and from this originate the excellent catalytic properties of this material.

Later on, the modification of the composition of the zeolite framework was extended to other elements, including Ga, V and, most important, B. The latter is quite interesting in zeolite synthesis because, contrarily to Ti, it can be incorporated into a variety of different structures. [10] Original synthesis procedures were developed for the preparation of crystalline microporous borosilicates ("boralites") with the **RUT** (BOR-A), **ANA** (B-analcime), **EUO** (B-EU-1), **FER** (B-ferrierite), **LEV** (B-levyne), Beta (BOR-B), **MFI** (BOR-C), **MFI/MEL** intergrowths (BOR-D, BOR-E), **MWW** (ERB-1) and **MTW** (B-ZSM-12) framework structures. [10] Several structural and spectroscopic evidences unambiguously assessed the real framework incorporation of this trivalent element, leading to conclude that B is the most versatile element for the isomorphous substitution of Al in zeolite frameworks. Among boralites, ERB-1 (**MWW**) proved to be particularly interesting because it was demonstrated for the first time the layered nature of its precursor, the ordered 3D structure being obtained by simple calcination through the condensation of Si-OH groups present on the surface of the layers. [11] Initially considered as a mere scientific curiosity, this finding has recently initiated the fruitful research line on the 2D zeolites that is now producing results of high interest. [12]

Alongside this activity, attention was also given to the optimization of the morphological characteristics of known zeolites used as catalysts in important petrochemical processes.
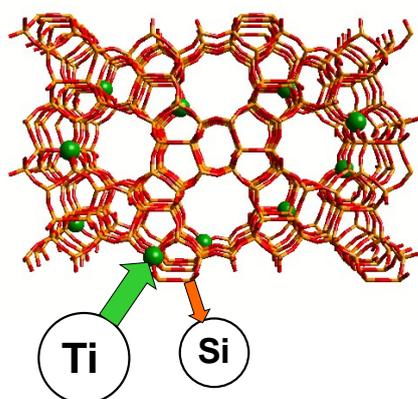

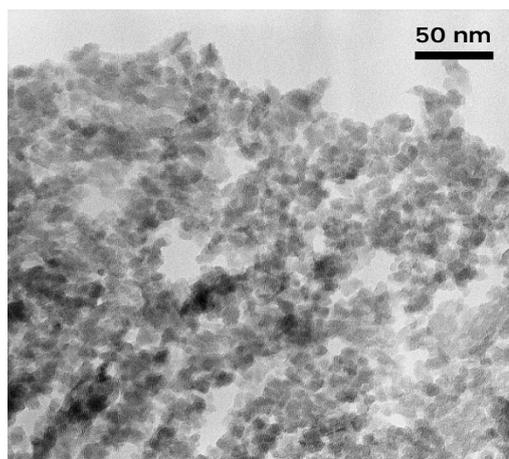**Fig. 1** Isomorphous substitution of Si by Ti in TS-1.

Fig. 2 Transmission electron micrograph of the zeolite beta catalyst employed in the cumene and ethylbenzene technologies.

It is the case, for instance, of the zeolite beta catalyst employed in the liquid phase alkylation of benzene with propylene to cumene and with ethylene to ethylbenzene, more extensively treated hereinafter. [13] The optimization of the synthesis conditions led to the preparation of samples composed by sub-micronic berry-like aggregates of very small crystallites (15 nm average dimensions), ideal morphology for the heterogeneous catalysts (Fig. 2).

It is worth noting that these aggregates, formed by crystallites of very small dimensions and with large mesoporosity resulting from their assembly, constitute a system with hierarchical porosity. This anticipates by some years another fruitful research line, precisely dedicated to the generation of different interconnected levels of porosity within the crystals/aggregates, necessary for eliminating the diffusional limitations normally affecting large zeolite crystals. Similar results were achieved in the case of the ZSM-12 catalyst *a priori* selected as a catalyst for the alkylation of naphthalene to 2,6-dimethylnaphthalene. [14]

Regarding the preparation of new zeolite structures, the efforts were focused on the role of organic additives (SDAs), selecting new families of compounds relatively simple and easy to synthesize. In this way, two new small-pore zeolites were prepared: ERS-7 (**ESV**) N,N-dimethylpiperidinium[15,16] and ERS-18 (**EEI**)[17] with N,N-dimethylpiperidinium hydroxide and 6-azoniaspiro-[5,5]-undecane hydroxide as SDAs, respectively. Interestingly, the ordered ERS-18 phase was discovered during the screening of the influence of the different synthesis parameters on the structural characteristics of ERS-10, a family of zeolites resulting from the intergrowth of **EUO**-**NES**-**NON** frameworks, which crystallizes with the same SDA. [18]

Finally, it is worth to mention the most recent research topic, still ongoing, aimed at preparing crystalline hybrid organic-inorganic metallosilicates, called Eni Carbon Silicates (ECS). Born in the wake of the strong interest in the preparation of mesostructured hybrid materials, particularly that prepared by S. Inagaki using 1,4-bis-triethoxysilylbenzene (BTEB) as a hybrid source of silica,[19] we have approached the problem in a rational way, trying to find the conditions that favour the arrangement of the disilane units in an ordered 3D structure. Decisive in this regard was the addition of a source of trivalent metal ions

(NaAlO$_2$, Ga(i-OC$_3$H$_7$)$_3$) to the reactant mixture and the accurate control of the reaction temperature, which must be maintained around 100°C to avoid the unwanted hydrolysis of the Si-C bond and the consequent crystallization of conventional low-silica zeolites. [20-25]

A number of different crystalline ECS phases have been synthesized so far and for some of them the crystal structure has been determined, allowing the definition of the main characteristics of these materials. Briefly, the structure of ECSs consists of a regular stacking of covalently bonded organic and inorganic layers, the latter being formed by [M^{3+}O$_4$] tetrahedra bonded, in some cases, to four different [O$_3$SiC] tetrahedra, in others to three [O$_3$SiC] and one [SiO$_4$] tetrahedra, without any Al-O-Al linkage. The Si/Al molar ratio is quite low, ranging from 1.33 to 2.00, and the negative charge is compensated by extra-framework alkali metal ions, mainly located inside the inorganic region. They can be exchanged by other alkali metal ions but not by the proton and this constitutes a limit for the possible application of ECSs as acid catalysts. Interestingly, the structure of the inorganic layers can be built by Secondary Building Units (SBUs) commonly found in zeolites and, in some cases, there are close relationships with known zeolite frameworks. For example, ECS-14 can be considered as the hybrid counterpart of aluminophosphate AlPO-5 and of SSZ-24 (its purely silica counterpart), both having the **AFI** framework type (Fig. 3). [22] Similarly, the inorganic layers of ECS-13, prepared with 2,6-bis-triethoxysilylnaphthalene (BTEN), have strong similarities with the AlPO-D (APD) framework. [23] In summary, from the spectroscopic and structural evidence collected so far, it is possible to conclude that ECS and related materials that are produced by other research groups can be classified as real hybrid organic-inorganic zeolites. [26]

At the end of this brief summary, it must be pointed out that the considerable resources devoted to the synthesis of new materials derive from the belief that innovation in processes and products cannot be separated from the availability of a large portfolio of proprietary materials. This has been the key of success for the development of the new processes described below.
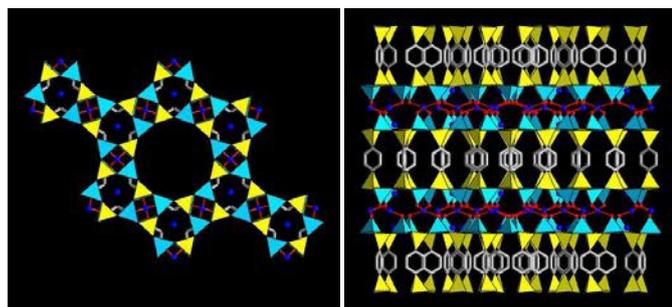

Fig. 3 [001] (left) and [110] (right) projections of the structure of ECS-14 ([AlO$_4$] light blue tetrahedra, [O$_3$SiC] yellow tetrahedra, phenylene rings grey hexagons, Si/Na tetrahedral sites blue balls).[22]

Zeolite catalysis

Selective oxidations by TS-1

One of the most important industrial achievements in the field of liquid-phase selective oxidation has been the discovery of TS-1. Thanks to its unique catalytic properties, several innovative processes that use hydrogen peroxide (H$_2$O$_2$) as oxidant are industrially applied. Today, more than 30 years after the discovery of TS-1, industrial processes are well developed and present in the technology portfolio of Versalis (formerly EniChem), a chemical company wholly owned and controlled by Eni S.p.A.

A vast literature is available on TS-1 material and catalysts, with detailed discussions on synthesis, characterization and catalytic properties. It is now well assessed that the exceptional catalytic properties of TS-1 are strongly connected to the presence of isolated, tetrahedrally coordinated Ti ions incorporated in the zeolite framework (Fig. 1). [4-8,27,28]

Selective oxidation with hydrogen peroxide

A very successful approach to selective oxidations is the use of oxygen donors, such as hydrogen peroxide (H$_2$O$_2$), hydroperoxides, organic peracids, nitrous oxide (N$_2$O), hypochlorites, etc. Among them, H$_2$O$_2$ is by far the most versatile, environmental friendly and the easiest to use. Furthermore, its price is relatively low, its active oxygen content (i.e. the amount of oxygen which can be delivered to the substrate) is very high (47 wt%) and the co-produced water has no environmental or safety drawbacks.

The availability of an industrial process for producing TS-1 allowed the development of several selective oxidations, all using H$_2$O$_2$ under mild conditions. Among them, the epoxidation of propylene (Hyprox process), the hydroxylation of phenol and the ammoximation of cyclohexanone are today industrially applied; even the hydroxylation of benzene to phenol has been thoroughly studied without finding, however, any practical application.

Propylene epoxidation. Propylene oxide is particularly important, since it is a basic intermediate with a production capacity of around 7×10^6 t/y.[29] Its classical industrial production routes are the chlorohydrin process (hydrochlorination of propylene with HClO followed by the reaction with a strong base (NaOH, Ca(OH)$_2$) or the direct epoxidation of propylene with a hydroperoxide. Although efficient and well consolidated, these methods suffer from a major drawback: the formation of high amounts of co-products. For instance, in the chlorohydrin process, 2.1 t of calcium chloride, dissolved in large volume of water and polluted by chloro-organics, are produced per t of propylene oxide. For this reason, the epoxidation of propylene with hydrogen peroxide, made possible by the TS-1 catalyst,[30,31] is particularly attractive: the only co-product is water and no chlorinated by-products are formed.

Clerici *et al.*[30] showed that when the reaction is carried out in methanol/water solution the conversion and the selectivity are high. After 90 min, 95% of the hydrogen peroxide is consumed, with 90% selectivity to propylene oxide. Propylene glycol and its monomethyl ethers are the main by-products, while the decomposition of hydrogen peroxide to oxygen is negligible. Catalytic activity decreases along with time on stream, while product distribution changes only slightly: it has been reported

that calcination at 550 °C is an efficient treatment to restore the initial catalytic activity. Washing with solvents (methanol or methanol/water mixture) somewhat above the reaction temperature, may also regenerate TS-1.

Paparatto *et al.*[32,33] reported that controlling the acidity with traces of buffering agents allows to increase the propylene oxide selectivity up to 98%. At the end of the reaction, the unreacted propylene, the epoxide and methanol are recovered by distillation, whereas the residual aqueous solution can be treated in an ordinary biological plant. No leakage of titanium has been observed under the reaction conditions. In 2001, the process was verified in a demo plant with a capacity of ca. 6 t/d built in Ferrara, Italy.[34]

In 2008, Dow and BASF successfully started up the first commercial-scale production plant based on the novel BASF/Dow HPPO (Hydrogen Peroxide for Propylene Oxide) technology at Antwerp, Belgium.[29] The technology uses a TS-1 catalyst. A second plant based on this technology began production in Map Ta Phut, Thailand, in 2011.

Another industrial-scale HPPO plant, licensed jointly by Evonik Industries and ThyssenKrupp Industrial Solutions, was built by SKC in Ulsan, South Korea, it has been in successful operation since 2008 a capacity of 100,000 t/y,[10] following increased to 130,000 t/y. The catalyst system utilized is based on a specifically developed and custom tailored TS-1 from Evonik.

Phenol hydroxylation. Hydroquinone and catechol are interesting chemical intermediates, used in the syntheses of several antioxidants. Besides, they also have specific uses: hydroquinone in the photographic industry, and catechol for the production of synthetic vanillin and other artificial aromas. In 2002, the production capacities were ca. 47,000 and 32,000 t/y, respectively.[35]

Historically, both hydroquinone and catechol were produced by several stoichiometric reactions aimed at transforming functional groups already present on the aromatic ring. One critical issue related to these processes is the low atom efficiency,[36] due to the stoichiometric consumption of reactants (e.g., NaOH, Cl_2, H_2SO_4) and oxidants or reductants (e.g., MnO_2, Fe), and the co-production of salts and oxides (NaCl, $MnSO_4$, FeO, Fe_2O_3). In particular, the production of hydroquinone has often been used as an example of old stoichiometric methods to be replaced by catalytic ones. A major improvement occurred with the development of the hydroxylation of phenol with H_2O_2 catalysed either by iron salts (Brichima process) or by strong mineral acids (H_2SO_4, H_3PO_4; Rhone–Poulenc process).[35]

In 1986, a new process for the hydroxylation of phenol with H_2O_2, catalysed by TS-1, was industrially applied by EniChem, which built a plant in Ravenna, Italy, for producing 10,000 t/y of the catechol/hydroquinone mixture. In the process, the reaction is run in a slurry reactor, at reflux in aqueous acetone or methanol. The catechol/hydroquinone ratio is in the range 1.1 : 1.2 and is strongly affected by the type of solvent.[37] The TS-1 catalyst provides good yields, thus making possible the operation at a phenol conversion of around 30%, significantly higher than that of the Brichima or the Rhone-Poulenc processes (9 and 5%, respectively), still maintaining selectivities higher than 80–85 and 90% based on H_2O_2 and phenol, respectively.[35]

Benzene hydroxylation. Phenol is one of the most important intermediates of the chemical industry. The global capacity for its production was more than 10 Mt/y in 2011, but with the new plants under construction in Asia, it will reach an overall capacity of 13 Mt/y in 2016. About 40% of the produced phenol is employed for the synthesis of Bisphenol A, a monomer for polycarbonates. Another 30% is consumed in the production of phenolic resins. The most important route for the industrial production of phenol is, by far, the cumene (iso-propylbenzene) process, which accounts for 98% of the installed capacity. The cumene process is based upon the researches of Heinrich Hock on the formation and decomposition of cumyl hydroperoxide [38] and is sometimes referred to as the Hock process. It comprises the Friedel–Crafts alkylation of benzene with propylene to cumene, followed by its oxidation with air to cumyl hydroperoxide, which is finally cleaved in acidic medium to get phenol and acetone (reaction 1):
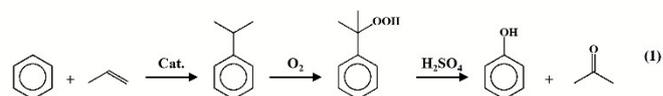
The major drawback of the cumene process is the co-production of ~0.6 t of acetone per t of phenol. Therefore, several efforts have been devoted to decouple phenol and acetone production and, particularly, to develop effective processes for the direct oxidation of benzene to phenol.

A first success in the direct of benzene oxidation was achieved with the development of the Solutia process. Discovered by Panov *et al.* at the Boreskov Institute of Catalysis (Novosibirsk, Russia) and developed in close cooperation with Monsanto, [39] this process uses nitrous oxide (N_2O) as oxidant and an iron-containing zeolite as catalyst. Though effective, it is unlikely that the Solutia process can become a major source of phenol due to the limited availability of N_2O, which is a by-product of adipic acid production, a chemical intermediate with a smaller demand with respect to phenol.

A promising alternative is provided by the direct hydroxylation of benzene with H_2O_2 catalysed by TS-1. [40,41] However, TS-1 does not perform very well in two-phase systems and only solvents able to homogenise the hydrophobic substrate and the aqueous H_2O_2 could be used. In the presence of solvents such as acetone, acetonitrile, and *tert*-butanol, the selectivity to phenol rapidly decreased even at low benzene conversion. Unexpectedly, however, conversion of benzene close to 8% and selectivity to phenol >80% were achieved by using sulfolane as a solvent. Even better results were obtained by a post-synthesis treatment of TS-1 with both H_2O_2 and ammonium hydrogen fluoride (NH_4HF_2). Upon such treatment (H_2O_2/F/Ti = 10/2.5/1; 60°C; 4 hours), a substantial amount of titanium (up to 75% of the initial value) was removed from the catalyst (named TS-1B) without affecting the crystalline structure of the zeolite and the catalytic activity. Even more important, at 8.6% benzene conversion, the benzene and H_2O_2 selectivities increased from

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83 to 94%, with catechol (4%) and hydroquinone (2%) as the only by-products. [40,41] To further increase the overall yield of the process, catechol and hydroquinone are treated with H_2 over a Ni-Mo catalyst and partially deoxygenated to phenol (Fig. 4). [42]
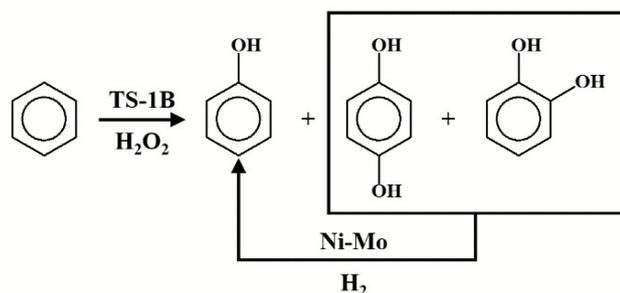

Fig. 4 TS-1 process for the direct oxidation of benzene to phenol.

The overall process performances, including hydrogenation section and the recycles, are: 100% benzene conversion, 97.7% selectivity on benzene and 71.0% selectivity on H_2O_2. However, economic evaluation performed on these data suggested that the direct oxidation of benzene by H_2O_2 is not yet competitive respect to traditional cumene process. [43]

Cyclohexanone oxime. Cyclohexanone oxime, prepared by ammoximation of cyclohexanone, is used for the synthesis of ε-caprolactam, an important intermediate (~ 4 Mt/y) for the production of nylon-6.

In the conventional synthesis route to ε-caprolactam (Fig. 5), cyclohexanone reacts with hydroxylamine sulphate to give cyclohexanone oxime. The latter then undergoes Beckmann rearrangement to ε-caprolactam in the presence of oleum. This route is penalized by the huge co-production of ammonium sulphate (4.4 t/t ε-caprolactam). [44]
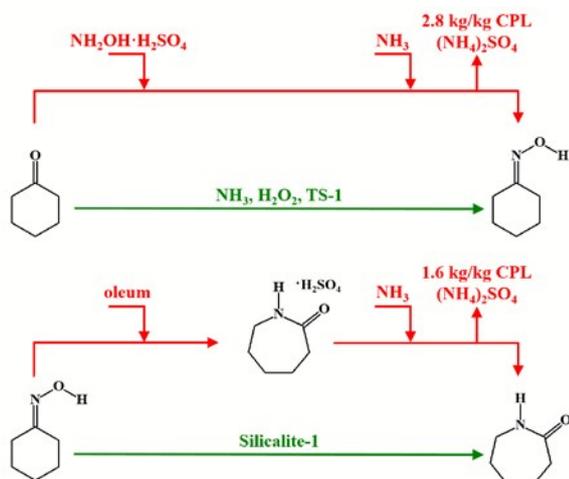

Fig. 5 Comparison of the classical (red arrows) and green (green arrows) approaches to ε-caprolactam synthesis.

An integrated process, which makes use of two **MFI**-type zeolite catalysts (TS-1 for the ammoximation of cyclohexanone and

Silicalite-1 (S-1) for the vapour-phase Beckmann rearrangement), is now industrially applied by Sumitomo for greener ε-caprolactam synthesis, without co-production of ammonium sulphate (Fig. 5). [45]

The EniChem process to cyclohexanone oxime is based on the reaction of cyclohexanone with NH_3 and H_2O_2 in the presence of TS-1 as a catalyst. Its advantages consist in the complete elimination of the problems related to the production and use of hydroxylamine and to the co-production of ammonium sulphate. The Beckmann rearrangement in the vapor phase, developed by Sumitomo, is based on the transposition of cyclohexanone oxime to the corresponding lactam, without the co-production of ammonium sulphate. High silica MFI zeolites, exhibiting a weak acidity, are suitable catalysts for this vapor-phase reaction. [45-50] Combining these processes, in 2003 Sumitomo realized a commercial unit for the production of ε-caprolactam in Ehime, Japan, increasing the existing capacity from 93,000 to 160,000 t/y. [29]

Aromatic alkylation, transalkylation and isomerization

Ethylbenzene (EB). In 2008 the world production capacity of EB was ~26 Mt, almost completely used for the production of styrene, a raw material for thermoplastic polymers and elastomers.

The original process for the production of EB was developed around 1930. The liquid-phase reaction is carried out in an agitated reactor (enameled or glass lined, to avoid corrosion) with $AlCl_3$-HCl as homogeneous catalyst, under somewhat gentle conditions (170°C and 0.7 MPa). The polyethylbenzenes (PEB, mainly diethylbenzenes, DEB), deriving from the consecutive alkylation of EB, are recycled back in the alkylation reactor where they undergo transalkylation with benzene, present in excess, reaching a conversion close to the thermodynamic equilibrium. The equilibrium composition is a function of the ratio of ethylene/benzene, which is typically in the range $0.35 - 0.55$. [51]

EB processes catalysed by zeolites. In order to overcome the problems related to the use of homogeneous acid catalysts, starting from the mid-1960s, different zeolite catalysts were proposed. In 1976, Mobil-Badger started up the first industrial plant for the production of EB in the gas phase, with a fixed-bed reactor, loaded with a catalyst based on ZSM-5. [52] The reactor is operated under high temperature (390-450°C) and pressure (1.5-2 MPa) conditions. As in the process with $AlCl_3$-HCl, after separation, the PEB are recycled back to the reactor for transalkylation. Due to the deactivation related to the deposition of heavy by-products (coke) in the zeolite pores, the catalyst must be regenerated quite frequently (i.e. every 40-60 days). This process, used commercially from 1980 onwards, was successively improved by the addition of a reactor dedicated to the transalkylation of the PEB, thus increasing both the EB yield and the catalyst life.

A considerable improvement with respect to these processes was later obtained by UOP/Lummus/Unocal with the development of a process operating in the liquid phase. The advantage of the liquid phase is represented by better thermal

control with the consequent extension of the catalyst life. In this way, the regeneration of the catalyst, performed *ex situ* with dedicated ovens, is less frequent. Due to problems related to diffusion limitations, medium-pore zeolites such as ZSM-5 were not suitable for liquid-phase processes. For this reason, in 1979 Unocal patented the use of large-pore Y zeolite as catalyst for the liquid phase alkylation of benzene with ethylene. [53] The process was commercially used for the first time in Japan in 1990.

Other large-pore zeolites proved to be suitable for the liquid-phase reaction (e.g. zeolite L, Omega, ZSM-12, Beta). As a result of these investigations in the early 1990's zeolite Beta was claimed to show the best performances independently by Innes *et al.* [54] and by Cavani *et al.* [55] The zeolite Beta showed higher selectivity than the Ultra-Stabilised Y zeolite (USY), with an overall selectivity (EB+PEB) of 99.3% against 91.1% of USY. [56]

Later on, very interesting results were obtained with MCM-22, a zeolite of medium pore size, which showed a catalytic activity comparable to USY, but inferior to that of Beta. However, the selectivity was higher with respect to both USY and Beta, since the formation of PEB was particularly low. [57]

The zeolite Beta is the catalyst developed by EniChem for its proprietary EB technology. [58] The catalyst was first used in an industrial reactor of an existing EB plant, starting from 2001. It showed exceptional performance in terms of both consumption of raw materials and quality of the EB produced. The catalyst was distributed in the reactor on several beds and the supply of ethylene was splitted over them in order to create a much higher local benzene/ethylene ratio with respect to the global one; in this way, the consecutive alkylation reactions to PEB were limited. [59]

Already in 2004, the majority of the 70 plants operating in the world were operated with zeolite catalysts and less than 20% were still using AlCl$_3$-HCl. [60]

Isopropyl-benzene (cumene). World production of cumene, almost exclusively used as intermediate in the synthesis of phenol, in 2012 was 13.1 Mt with an installed capacity of ~14.7 Mt/y. The demand of cumene is expected to grow to >18 million t in 2020, as a consequence of the increase of the consumption of phenol (from ~10.0 Mt in 2012 to ~14.2 Mt in 2020, corresponding to 4% yearly growth).

The alkylation reaction of benzene with propylene is very similar to that with ethylene: propylene reacts with benzene to give cumene and by successive alkylations to give di- (DIPBs) and tri-isopropyl-benzenes (TIPBs). After separation, DIPBs and TIPBs are transalkylated with an excess of benzene to increase the overall yield of cumene. Other undesired side reactions may occur, the most important being the propylene oligomerization to long-chain olefins that, in turn, may undergo cracking to light products or may alkylate benzene reducing the overall selectivity and yield of cumene. Moreover, isomerization of cumene leads to small but significant amounts of *n*-propylbenzene (nPB). This represents a very critical aspect, as nPB cannot be separated by simple distillation and thus its formation affects the final quality of the cumene, even if present at a level of few hundreds ppmw. [56]

The pioneering process for the production of cumene was introduced during the Second World War, in order to satisfy the demand for cumene as a high-octane additive for aviation fuels. This process used sulphuric acid as catalyst, with all the problems related to the use of a free mineral acid. These drawbacks were overcome in the 1940s, when UOP introduced a new heterogeneous acid catalyst, i.e. phosphoric acid supported on kieselguhr (SPA). The success of this technology is demonstrated by the fact that in 1994 (i.e. after 50+ years from the first commercialization), the majority (75%) of the cumene plants still operated with SPA catalyst. Its use requires to work with a large excess of benzene (molar ratio C$_6$H$_6$/C$_3$H$_6$ = 5 − 10) in order to limit the formation of polyalkylates (that are not transalkylated by SPA) and of propylene oligomers. Apart from that, SPA catalyst has some unresolved drawbacks: it generates corrosion, due to a release of free acid from the support, and is impossible to regenerate.

In the 1970s, Monsanto-Lummus introduced a new technology based on the use of AlCl$_3$-HCl, very similar to that used for EB with the possibility of recycling polyalkylates into the alkylation reactor, as AlCl$_3$ possesses transalkylation activity, in contrast to the SPA catalyst. However, only a few plants have been realized with this technology. [58]

Cumene processes based on zeolite catalysts. The development of zeolite catalysts for the production of cumene has been quite similar to that for EB, but more time and efforts were required. This was mainly due to the low selectivity of zeolite ZSM-5, the catalyst for Mobil-Badger's EB process, that favours the formation of large amounts of nPB. On the other hand, ZSM-5, as medium-pore zeolite, is not sufficiently active in the liquid phase.[56] Also for cumene, a noticeable improvement was therefore obtained by operating in the liquid-phase with large-pore zeolites. [54,55] The use of zeolite catalysts for this reaction has been examined in details in some papers. [13,61-63] Combined experimental investigations and molecular mechanics and dynamics calculations on several zeolite structures (e.g. ***BEA**, **MOR**, **FAU**, **MTW** and **MWW**) allowed to conclude that zeolite Beta should be the best choice for liquid-phase alkylation of benzene with propylene. [13]
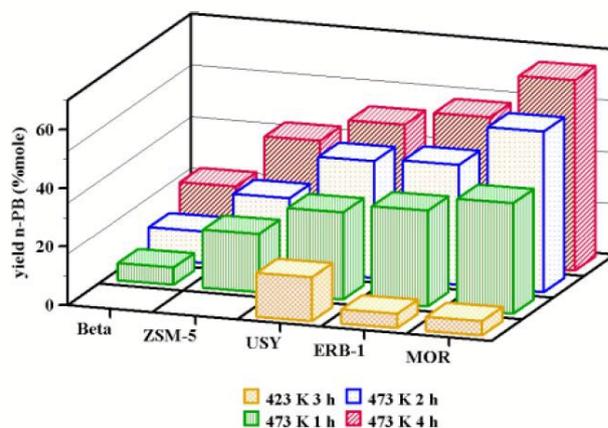

Fig. 6 Product yields for nPB**,** produced over H+ form zeolites.[64]

Slightly different conclusions were reached by Corma *et al.*, who found that MCM-22 (**MWW**) should be preferred over zeolite Beta, mainly because of its stability. [63] On the other hand, catalytic tests on cumene isomerization, showed that the formation of nPB increases in the following order: Beta < ZSM-5 (**MFI**) < USY (**FAU**) ≈ ERB-1 (**MWW**) < MOR (Fig. 6). [64]

In any case, large-pore zeolites proved to be suitable catalysts for the liquid-phase cumene production. During the years 1990s, this led to the realization of new commercial processes or industrial test runs based on the use of catalysts belonging to this family of microporous solids performed by Dow-Kellogg (modified Mordenite), Mobil-Raytheon (MCM-22), CDTech (Y), EniChem (Beta) and UOP (Beta). [65] Mobil-Raytheon, EniChem and UOP independently started-up industrial zeolite-based cumene plants in 1996. In 2002, more than 50% of the cumene production units were switched from older SPA-based processes to operate with zeolite catalysts. [65]

Cymenes (methylisopropylbenzene). Cymene is industrially produced by alkylation of toluene with propylene. Similarly to cumene, cymene is than oxidized and cleaved to produce cresols. Although the demand for cymene is much lower than for cumene, some commercial units are operating with an installed capacity of around 40 Kt/y. [58] The alkylation produces a mixture of *o*-, *m*- and *p*-cymene isomers, the o- being less desired because it is difficult to oxidize and inhibits the oxidation of the other isomers.

Two catalytic technologies, based on $AlCl_3$-HCl and on SPA, are employed. Using $AlCl_3$-HCl (liquid-phase, T=60-80 °C), an isomer ratio close to the thermodynamic equilibrium is obtained (i.e. 3% *o*-, 64% *m*-, and 33% *p*-cymene). [51] SPA process differs from $AlCl_3$-HCl process for the isomers distribution obtained, which is far from the equilibrium values (40% *o*-, 25% *m*-, and 35% *p*-cymene). The process has a separation unit (Cymex), based on a 13X molecular sieve, for the separation of *m*- and *p*- isomers, which allows the production of the corresponding pure cresols. [66]

Zeolite catalysts. The isopropylation of toluene with propylene or isopropanol was largely studied using different zeolite catalysts both in gas- and in liquid-phase.

In the liquid phase alkylation of toluene with propylene (T = 180 °C, P = 3.9 MPa), [67] zeolite Beta produces a low concentration of the *o*-cymene and a high *m*-/*p*-cymene ratio. Amorphous mesoporous silica-aluminas (i.e. MCM-41 and MSA) were also considered, showing an activity comparable to zeolite Beta, but lower cymene selectivity, because of the higher polyalkylates formation. The distribution of cymene isomers is similar to that reported for SPA. [67]

In conclusion, zeolite Beta is the best candidate to substitute $AlCl_3$-HCl for the liquid phase alkylation of toluene with propylene, while MSA and MCM-41 can be considered as a possible alternative to SPA catalyst.

2,6-dimethylnaphthalene (2,6-DMN). Polyethylene-naphthalate (PEN) is an interesting thermoplastic polyester prepared by co-polymerization of dimethyl-2,6-naphthalenecarboxylate (2,6-NDC) with ethyleneglycol. The most critical point in the PEN synthesis route is related to the availability of 2,6-DMN, which is firstly oxidized to the corresponding dicarboxylic acid and then esterified with methanol to 2,6-NDC. A promising route is the process based on

the methylation of naphthalene (NAPH) and methylnaphthalenes (MNs) over zeolite catalysts, briefly reviewed by Millini *et al*. [14]

The direct methylation of NAPH or MNs to DMNs leads to the production of 10 different isomers, which are rather difficult to separate because of the close boiling points. Examining the DMN isomers distribution at the thermodynamic equilibrium at 400°C, [68] one realizes that the β-positions are preferred over the α-. In addition, Pu and Inui [69] reported that the isomerization occurs within each of the following groups:

1,5-DMN – 1,6-DMN – 2,6-DMN (A)
1,8-DMN – 1,7-DMN – 2,7-DMN (B)
1,4-DMN – 1,3-DMN – 2,3-DMN (C)
1,2-DMN   (D)

Therefore, only the DMN isomers belonging to group A are considered interesting, since 1,5- and 1,6-DMN can be isomerized to the desired product. Furthermore the formation of 2,7-DMN should be avoided or, at least, limited: it is easily formed but, belonging to group B, neither it can be transformed in 2,6-DMN nor can be easily separated from it. Preliminary test of alkylation of NAPH with methanol showed that, in the presence of 1,2,4-trimethylbenzene (pseudocumene, TMB) as a solvent, the selectivity to 2,6-DMN, the 2,6-DMN/2,7-DMN ratio and the catalyst life were higher than without solvent. [60]

The most promising zeolite catalyst was selected through the application of molecular mechanics and dynamics calculations, which also limited the otherwise onerous experimental screening of the catalysts. Aim of these calculations was to predict the shape selectivity properties of several medium (**MFI** and **EUO**) and large pore (**MOR**, **MAZ**, ***BEA**, **FAU**, **LTL**, **OFF** and **MTW**) zeolites, by determining the minimum energy pathways (MEPs) for the diffusion of reactants (NAPH, 1-MN, 2-MN) and selected products (1,5-DMN, 1,6-DMN, 2,6-DMN, 2,7-DMN). [14]

The MEPs determined for all the molecules in medium-pore zeolites were characterized by high-energy barriers, indicating a rather difficult diffusion of all the molecules in the 10MR pores (Fig. 7). For this reason, the use of **MFI** and **EUO** (and by extension of all medium-pore zeolites) as catalysts for 2,6-DMN production was not advised.
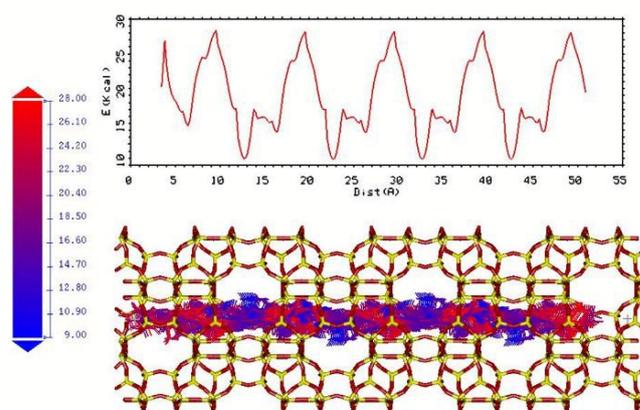

Fig. 7 MEP for 2,6-DMN in the straight 10R channel of MFI. From the energy plot, the barrier for the diffusion of 2,6-DMN is estimated 17.6 kcal·mol^{-1}. [14]

In the case of large-pore zeolites more diversified and interesting results were obtained. **MOR**, **MAZ**, *****BEA** and **FAU** were expected to be completely unselective, while high selectivity was argued for **OFF** and **MTW**. The latter, in particular, displayed a very interesting feature, i.e. the high energy barriers hampering the diffusion of the undesired 2,7-DMN isomer.

Indeed, the catalytic tests (performed at 350°C, with molar ratio TMB:NAPH:CH$_3$OH = 10:1:3 on the two medium-pore zeolites [H-ZSM-5 (**MFI**) and H-EU-1 (**EUO**)] and on some of the large pore zeolites considered in the simulations [H-Mordenite (**MOR**), H-Mazzite (**MAZ**), H-Beta, USY (**FAU**) and H-ZSM-12 (**MTW**)][70] confirmed the predictions of the theoretical calculations.[14] **MTW** was therefore selected as the most promising zeolite catalyst for 2,6-DMN production and on this zeolite was based the development of the EniChem process tested at a pilot plant scale. [71]

Mesitylene and Durene. Mesitylene (1,3,5-trimethylbenzene – 1,3,5-TMB) and durene (1,2,4,5-tetramethylbenzene – 1,2,4,5-TeMB) are important raw materials for the preparation of trimesic and pyromellitic acids, in turn used in the production of plasticizers. 1,3,5-TMB and 1,2,4,5-TeMB are contained in limited amounts in the reformate streams of naphtha reforming from which they are difficult to recover. Alternatively, starting from pseudocumene (1,2,4-trimethylbenzene – 1,2,4-TMB), contained in relatively large amounts in same reformate streams, it is possible to obtain 1,3,5-TMB and 1,2,4,5-TeMB via acid-catalysed isomerization/disproportionation. Shape-selective catalysts are required for enhancing the selectivity to mesitylene and durene. These reactions have already been examined by several authors, using different zeolites (e.g. ZSM-5, NU-87, MCM-22 as medium-pore zeolites; Y , Beta and Mordenite as large-pore zeolites). [72] A computational study aimed at screening the potential zeolite catalysts useful for these reactions was undertaken. The computational approaches were those employed in the selection of zeolite catalysts for the synthesis of 2,6-DMN and included the determination of the MEP, location and energetics of all the TMB and TeMB isomers in a number of medium-pore (**MFI**, **EUO**, **MWW**, **NES**) and large-pore (*****BEA**, **FAU**, **MOR**, **LTL**, **MAZ**, **MTW**, **OFF**, **IFR**, **ISV**) zeolites. The outcomes of this study helped the selection of the zeolite catalysts for simultaneous isomerization and disproportionation. Properly combining this reaction step with separations (e.g. distillations and crystallization) and recycle, an optimized process for the production of mesitylene and durene from pseudocumene has been defined. [73]

Condensations of ketones and aldehydes with aromatics

The condensation of molecules containing carbonyl groups, such as aldehydes and ketones, with aromatic compounds is a reaction applied in the chemical industry to produce important commodities such as Bisphenol A and methylendianiline.

Bisphenol A (p,p'-isopropylidenediphenol) (BPA) derives from the acid-catalyzed condensation of 2 moles of phenol with 1 mole of acetone. World capacity of BPA is 2.67 Mt/y (2001) and the product is mostly used for the production of polycarbonates epoxy resins. [74]

Methylendianiline (MDA) derives from the reaction of 2 moles of aniline with 1 mole of formaldehyde and is used as a precursor of methylendiisocianate (MDI). In 2000, the world production of MDI amounted to more than 2 Mt. [74]

Zeolite catalysts for BPA production. The use of zeolites (e.g. X and Y) as acid catalysts for the production of BPA was claimed in 1970 by Mobil Oil Corporation. [75] The conversion reported in the patent were however too low. Later on, Nowinska and Kaleta, reported that, for the same reaction, H-ZSM-5 mainly produced alkylated phenol and mesityl oxide, with very low phenol conversion. These results can be explained with the narrow pore size of ZMS-5, which hampers the formation of the bulky products deriving from the condensation of phenol and acetone. [76] On the contrary, large-pore zeolites with spaciousness index [77] greater than 8 were claimed to be good catalysts for BPA synthesis (Fig. 8). [78] The best results were obtained with zeolite Beta: in this case complete acetone conversion and 49% and 27% selectivities to BPA and o,p'-BPA, respectively, were reached. An interesting property of these zeolite catalysts is that they can be completely regenerated by treatment with a specific solvent at a temperature preferably higher than the reaction one (process known as rejuvenation). [74]
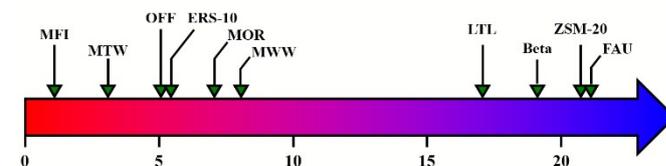

Fig. 8. Spaciousness indexes of different zeolite structures.[74]

Zeolite catalysts for MDA production. The substitution of HCl with solid catalyst in the MDA process is highly desirable, avoiding the production of brines contaminated with aromatic amines, which need special treatments before being disposed. In the 1990s, several zeolites, such as Y, ZMS-5 and Silicalite-1 isomorphously substituted with Ti, B or Fe, were claimed to be active catalysts in MDA synthesis. [79] However, as in the case of BPA, the best zeolite catalysts were selected according to their spaciousness index (SI): zeolites with a SI between 2.5 and 19 were reported be the most active in MDA synthesis. Among them, the best results were obtained using Beta and ERB-1 (MWW), since they led to a complete aminal conversion. [80] Reaction mixtures contained about 55-60% of MDA, 20-23% of o,p'-MDA, while the remaining part was constituted by trimeric and tetrameric products. Zeolite Beta gave a higher amount of o,p'-MDA than HCl (22.8 and 3-5%, respectively) as a direct consequence of the lower reaction temperature required by the mineral acid catalyst. [74] In order to solve this possible drawback, it was reported that the treatment of the zeolite surface with silylating reagents is effective to decrease the o,p'-MDA formation, increasing in the same time the MDA content in the products. [81] Treating the chosen zeolite either with organic silicon compounds of general formula Si(OX)$_4$ and especially

with octamethylcyclotetrasiloxane (OMTS), the *o,p*'-MDA content could be sharply reduced without lowering aminal conversion and the catalyst life. Reasonable explanations of the enhanced selectivity to MDA were both the inertness of the external non-selective zeolite surface and the narrowing of the pore mouth thus modifying the diffusional limitations experienced by the different molecules. [74]

Hydrodearomatization and related reactions

Improvement of gasoil properties by selective ring opening. Over the last two decades, the EU refining industry has faced significant changes in products demand both in terms of quality requirements and relative demand for gasoline and diesel. The enactment of increasingly stricter regulations concerning fuel quality might pose severe limitations to the use of high-aromatic streams in diesel fuel blending. Streams from, e.g., cokers and catalytic cracking units or from bitumen-derived synthetic crude oils, cannot have this destination if new upgrading processes are not introduced in the refining cycle. A possible option to increase middle distillate production is the increase in the light cycle oil (LCO) yields of fluidized catalytic cracking (FCC) units, together with its upgrading to products suitable for the diesel pool. [82] An approach, which potentially can lead to the highest achievable improvement in terms of yields, combustion characteristics of the products and environmental impact, is the saturation of the aromatic structures followed by the selective breaking of endocyclic C–C bonds of naphthenic structures so formed, to produce alkanes with the same number of C atoms as the starting molecule. As shown in Fig. 9, although accompanied by a high hydrogen consumption, the upgrading route achieves the complete ring opening of naphthenic structures with a significant improvement in the Cetane Number and a remarkable decrease of the soot formation tendency. [83] The Selective Ring Opening (SRO) has been actively investigated in the past ten years. [84-89]
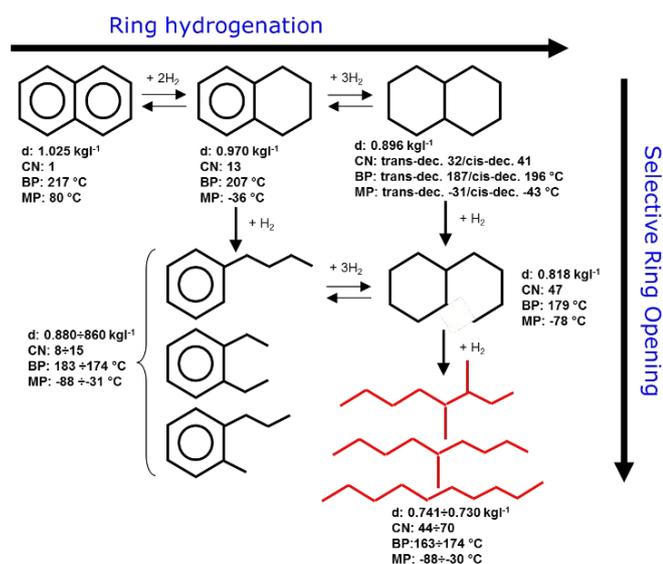

Fig. 9 Idealized network for ring-opening of poly-aromatic hydrocarbons into alkanes (adapted from Ref. 90).

The most widely employed model hydrocarbons are one ring ((alkyl)-cyclopentane, (alkyl)-cyclohexane) and two fused rings (naphthalene, 1-methylnaphthalene, tetralin and decalin); on the contrary, very few investigations have been carried out with three fused rings. In principle, SRO is a promising route to upgrade low-value feeds to high-quality products; however, its practical realization represents a challenge because this process is characterized by a complex chemistry, where not all effects of the different factors affecting the selectivity, the distribution and the composition of the products have been fully elucidated yet. The inherent difficulties in improving the Cetane Number of diesel fuels by SRO have been examined by Santana *et al.* [91] However, one limiting factor for the upgrading of refinery cuts is the relatively low selectivity for open chain alkanes upon conversion of naphthenic or benzo-naphthenic structures containing two or more fused rings. Until recently, only few publications reported the formation of open-chain decanes (few percent) from the hydro-conversion of C10 naphthenes.[92-94]

HIgh-PErformance Ring Opening Catalysts (HIPEROCs) for upgrading via selective ring opening. In order to evaluate the possibility of upgrading high-aromatic streams via selective ring opening, Eni and the University of Stuttgart carried out a collaboration project aimed at: (i) identify the key factors affecting the activity and selectivity for the breaking of endocyclic C–C bonds of naphthenic structures; (ii) develop catalytic systems with high selectivity towards the formation of open-chain paraffins. In order to fulfil the objectives, the effect of the kind of noble metals, the metal loading, the concentration/strength of Brønsted acid sites and the type of support were investigated. [95-97] As for the latter, different types of zeolites (FAU, Beta, MOR, etc.) as well as non-acidic supports (silica and [Si]SBA-15) were used. The results of the investigations carried out with model compounds (mainly decalin) evidenced that that among the metals tested (Pd, Pt, Ir, Ru, Re, Rh), Ir and Pt are the most suitable because characterized by the necessary balance between hydrogenolytic and hydro-dehydrogenating activities. Moreover, all the experimental evidences suggested that the balance between the metal content and the concentration/strength of Brønsted acid sites is crucial in determining the activity of the catalyst but, above all, their selectivity for open-chain paraffins. The best catalysts are those characterized by a relatively high hydrogenolytic activity and a low acid activity. Distinctive characteristics of HIgh-PErformance Ring Opening Catalysts (HIPEROCs), in comparison with classic bifunctional catalysts, are the high metal loading with good hydrogenolytic activity and low concentration/strength of the Brønsted acid sites. The main function of the Brønsted acid sites in HIPEROCs is the mild isomerization of 6-membered into 5-membered naphthenic rings, which are much easier to open by hydrogenolysis. The strength of Brønsted acid sites was modulated by adding different alkali metals as charge-compensating cations in the zeolite. [98-100] In the case of zeolites Y and Beta, clear evidence was obtained that either too strong or too weak Brønsted acid sites are detrimental for the selectivity to open-chain paraffins.

In the case of decalin conversion, too strong Brønsted acid sites, favour the undesired paring reaction of intermediate alkyl-substituted cycloalkanes over the hydrogenolytic ring opening of the latter to open-chain decanes. On the other hand, if the Brønsted acid sites are too weak, the isomerization activity with ring contraction of decalin is too low and the chemistry is mainly governed by direct ring opening of decalin by hydrogenolysis [101] of 6-membered naphthenic rings, which is characterized by a lower selectivity. The progress made in understanding the chemistry involved and the effect of the main factors affecting the activity and selectivity of the selective ring opening reaction, led to the recent introduction of a new family of ring opening catalysts. [98-100] They are made up of Ir- and Pt-containing zeolite Y and Ir-containing zeolite Beta with an unusually low concentration of Brønsted acid sites and a relatively high amount of noble metal (3 wt%). In addition, the strength of the Brønsted acid sites can be tuned by ion exchange with alkali metals: Na and Cs led to the best results for zeolites Y and Beta, respectively. The results showed that, by appropriate tuning of the [metal]/[Brønsted acid sites] ratio and strength of the Brønsted acid sites, it is possible to achieve unprecedented yields of open chain decanes (OCDs) up to ca. 45% during decalin hydroconversion.

The currently known HIPEROCs contain both noble-metal and Brønsted-acid sites and are thus members of the long-known family of bifunctional catalysts. They differ, however, substantially from the conventional noble-metal/zeolite catalysts industrially used in hydrocracking of vacuum gas oil 1[02,103] or in the isomerization of light gasoline. [104] In these conventional bifunctional catalysts, the main function of the noble metal is – beside prevention of coke formation and the concomitant catalyst deactivation – to promote the rapid interconversion of alkanes and alkenes by dehydrogenation/hydrogenation, [105,106] whereas the second main reaction catalysed by noble metals, i.e., hydrogenolytic cleavage of carbon–carbon bonds, [107,108] is mostly undesired. Consequently, noble metals with a relatively low activity for hydrogenolysis, such as Pd or Pt, are traditionally used in conventional bifunctional catalysts and the content of noble metal is low, typically below 1 wt.%. [109] At the same time, the concentration and strength of the Brønsted acid sites in these catalysts are relatively high, since these sites promote desired reactions, namely skeletal rearrangements and C–C bond cleavage via β-scission of the carbocations. [106,110] Differently from the conventional bifunctional catalysts, features of HIPEROCs include:
(i) a noble metal with a high activity for hydrogenolysis, e.g., Ir;
(ii) a higher metal content, e.g., in the range from ca. 2 to 4 wt.%;
(iii) a lower concentration and strength of Brønsted acid sites.
In other words, the optimal balance between both types of sites is fundamentally different in HIPEROCs and in conventional bifunctional catalysts. Also important for a HIPEROC is a as high as possible selectivity for cleavage of endocyclic bonds compared to that of exocyclic C–C bonds in alkyl side chains, because only the former results in the desired ring opening with retention of the carbon number. On conventional bifunctional

catalysts, with their relatively low activity for hydrogenolysis and their strong acid component, cleavage of endocyclic bonds is very slow compared to β-scissions of exocyclic C–C bonds in alkyl side chains. [107]

Tests with Dearomatized LCO. The results of the studies with model compounds showed that, by carefully tuning the support acidity and concentration of the metal, it is possible with zeolites Y and Beta to obtain high yields of open-chain decanes during the hydroconversion of *cis*-decalin. With the proper catalytic system, the desired ring opening reaction can be maximized, limiting two undesired competing reactions of ring opening products (ROPs):
(i) the hydrogenolysis of exocyclic C–C bonds in the alkyl side chain(s). For selective ring opening of decalin to occur, a hydrogenolysis component in the catalyst and proper reaction conditions are needed, which favour as much as possible cleavage of endocyclic over that of exocyclic C-C bonds;
ii) the "paring reaction" which is acid-catalysed and consists of a series of skeletal type A (non-branching) and type B (branching) rearrangement steps followed by a rapid type A β-scission of α,γ,γ-tribranched carbenium ions. [106,112-114] Starting from any C10 one-ring naphthene, it leads to the products *iso*-butane and methylcyclopentane. If OCDs are the desired products, the paring reaction has to be suppressed to the maximum possible extent by reducing the concentration and/or strength of the Brønsted-acid sites of the catalyst. The occurrence of the paring reaction or not can be easily monitored by measuring the C-number distribution of the C9-products: If the paring reaction is involved, M-shaped distribution curves result in the region C3 to C7 with sharp maxima at C4 and C6, as demonstrated, for example, in Ref. 112 for decalin hydroconversion on Ir/La-X zeolite. The good results obtained with *cis*-decalin make these catalysts good candidates for the upgrading of real refinery feeds. An experimental campaign with a refinery feedstock was carried-out in order to test the catalyst under "real" operating conditions. A LCO fraction, coming from a refinery FCC unit was used. The feed was pre-hydrogenated in two steps: first at hydrodesulfurization operating conditions (T = 330°C, P = 75 bar, LHSV: 1 h^{-1}), then at dearomatization conditions (T = 250 °C, P = 70 bar, LHSV: 1 h^{-1}) in order to eliminate the mono-aromatic molecules. This pretreatment step should be considered in the development of the SRO industrial process when starting from high-aromatics feeds. The results obtained with 4.0%Pt/Na0.88,H0.12-Y show that with increasing conversion, the composition of dearomatized LCO undergoes deep changes (Fig. 10). [98-100] Particularly, condensed naphthenic structures undergo a strong decrease while alkanes and alkylsubstituted one-ring naphthenic structures show a steady increase. In both cases, at 80% gasoil yield, a decrease of naphthenic structures with two or more condensed rings of about 70% is observed while the paraffin content passes from 22% up to 40%. The observed trend is consistent with a pathway of consecutive reactions, where the more condensed naphthenic structures are progressively converted into less condensed structures up to the formation of alkanes. The process is of course

accompanied by the formation of cracking products as witnessed by the lower yields of the gasoil fraction. However, it should be noted that the cracking yields are relatively low in comparison with the profound changes in molecular structure undergone by the DeAr-LCO.

As shown in Fig. 11, the changes of molecular structure occurring during hydroconversion leads to a progressive increase of the Cetane Index as a function of degree of conversion. At 80% of gasoil yield, the increase of the Cetane Index was of 11 units. The observed increase is consistent with the Cetane Number reported in the literature for the different classes of hydrocarbons showing the following order: alkanes > alkyl-cyclohexanes > alkyl-decalins > alkyl-naphthenes with more than three condensed rings. [115,116]
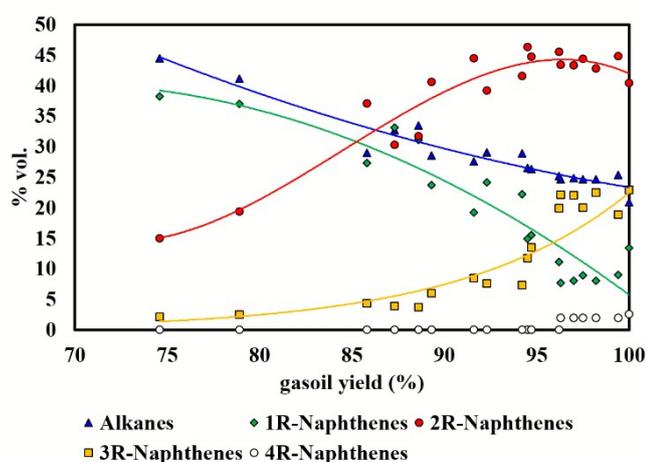

Fig. 10 Changes of chemical structure during hydroconversion of DeAr-LCO over 4.0%Pt/Na0.88, H0.12-Y. The prefixes 1R, 2R, 3R and 4R stand for naphthenic structures with 1, 2, 3 and 4 condensed rings. (Reprinted from ref. 99 with permission of Elsevier)
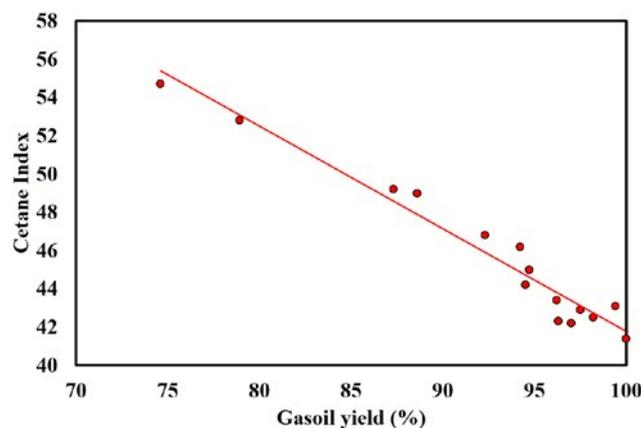

Fig. 11 Cetane Index of hydroconversion products of DeAr-LCO over 4.0%Pt/Na0.88,H0.12-Y.

Use of zeolites in separation processes

Zeolites have found application for both gas and liquid-phase separations taking advantage from their peculiar features: i)

high selectivity due to strictly defined structure; ii) tunable polarity; iii) proven stability; iv) excellent regenerability. [117]

Zeolites as gas adsorbents for the oil and gas industry

Natural gas (NG) share of the global energy demand is foreseen to grow for the next decades. [118] Such scenario is due to: i) implementation of more efficient transportation systems; ii) remarkable reserves found; iii) NG clean-burning characteristics.

Raw NG is collected at wellhead as a mixture containing a wide range of compounds in addition to methane (e.g., condensable hydrocarbons, water, sulphur compounds, carbon dioxide, nitrogen, mercury compounds, silicon compounds, helium). According to that, NG conditioning is needed to lower contaminant content until specifications imposed by downstream processors. [119] Zeolites are effectively implemented in gas separation processes based on sequences of adsorption and regeneration operations. [120] Differences in adsorption thermodynamics and kinetics among mixed compounds make separation feasible, once identified adsorbent or adsorbents combination with adequate selectivity, capacity and regenerability. Two main regeneration approaches can be adopted: i) heating in temperature-swing-adsorption (TSA) processes; ii) de-pressurisation in pressure-swing-adsorption (PSA) processes. [121]

FAU and **LTA** aluminium-rich zeolites are extensively used in NG conditioning due to their effectiveness and acceptable cost of about 10 USD/kg. They are applied for trace removal, respectively, of condensable hydrocarbons and polar compounds (e.g., water, carbon dioxide, sulphur compounds). Regeneration is performed by heating at about 300 °C, due to the strong adsorbate-adsorbent interaction.

Aluminium content has been identified as the key feature to be considered for tuning the magnitude of adsorbate-adsorbent interaction in zeolites. An optimal trade-off between selectivity towards polar compounds and regenerability under mild conditions has been found for siliceous materials. [122-124] According to that, porous silica and silica-alumina are considered as alternative adsorbents, for NG conditioning, allowing regeneration at temperatures slightly lower than those needed for aluminium-rich zeolites (about 250 °C vs. 300 °C). [125] Furthermore, laboratory-scale experimentation has pointed to Eni ERS-8 porous silica-alumina as an adsorbent applicable in PSA processes for the removal of carbon dioxide or hydrogen sulphide from sour NG. [126-128]

The adsorption isotherms acquired at 30 °C with pure hydrogen sulphide, carbon dioxide and methane on ERS-8 silico-alumina are reported in Fig. 12. The preferential adsorption of both hydrogen sulphide and carbon dioxide over methane is evident. Furthermore, the adsorption isotherms are almost linear. This behaviour allows the massive adsorption by ERS-8 of NG acid contaminants and their desorption by pressure reduction, according to a PSA strategy.

Zeolites as adsorbents for water remediation

Global water crisis is one of the main drawbacks of fast economic growth. It has been estimated that nearly 80 % world

population is exposed to high levels of threat to water security. [129] In this context, water remediation is a major challenge.

Groundwater contamination is an issue due to ineffective waste management, widespread dispersion of chemicals or natural release of noxious compounds from rocks and soils. Two main groundwater remediation approaches can be employed: i) groundwater can be pumped to surface treatment facilities, following the pump-and-treat (P&T) option; ii) permeable reactive barriers (PRBs) can be exploited. In the latter case, beds of active material are sunk into plume, forming active cells where contaminants are trapped or converted into non-hazardous compounds. [130] Zeolites have drawn interest due to their both verified and potential effectiveness as adsorbents for water remediation. [131]

Natural zeolites (mainly clinoptilolite) are available in large quantities in mineral deposits. According to that, they are considered low cost adsorbents being quoted less than 1 USD/kg. They are generally aluminium-rich, thus polar. Indeed, cation-exchange is one of their oldest applications. [132] Cation-exchange thermodynamics has been detailed, pointing to key features determining zeolite performance: i) zeolite framework structure; ii) zeolite framework electrostatic field strength; iii) cation charge density; iv) contacting solution composition; v) contacting solution pH; vi) raw mineral composition and work-up; vii) process apparatus and operating conditions. [133]

Zeolite affinity towards anions and non-dissociated compounds is by far lower, requiring adsorbent modification or at least, careful selection. [134] Encouraging results concerning both anions and non-dissociated compounds removal have been referred for adsorbents based on natural clinoptilolite zeolite modified with bulky alkyl-ammonium surfactants. Such surface-modified zeolites (SMZs) have been effectively implemented until pilot-scale according both to PRB [135] and P&T [136] approaches. Minimal influence of surface modification on cation-exchange features has been shown.[137] According to that, SMZs has to be considered as multi-purpose adsorbents able to get: i) cations at zeolite framework exchange sites; ii) anions by interaction with surfactant molecule hydrophilic cationic heads; iii) non-dissociated compounds by partitioning into surfactant molecule hydrophobic tail bundles.

Effective regeneration by air sparging has been experimented for SMZs exhausted with volatile organic non-dissociated compounds while any regenerability approach of SMZs exhausted with inorganic salts has not defined. Additionally, relevant surfactant leaching has been witnessed. [138]

Siliceous zeolites have been suggested to front this drawback. Effectiveness of silicalite, mordenite and Beta siliceous zeolites as adsorbents for non-dissociated compounds has been tested through both laboratory- and demonstrative-scale [139] experiments. Zeolite performance has been verified to be better than active carbon one in term of both specific capacity and stability under harsh conditions. [140] The En-Z-Lite[TM] process developed by Eni entails the use of siliceous zeolites in both PRB and P&T systems. Results from one-year experience concerning a PRB built under a coastal refinery have been described, evidencing zeolite structural stability. [139,141]

The system was able to treat until over 8 m³/day of groundwater. Organic contaminant concentration upstream the system was almost constantly of 5 mg/L for total petroleum hydrocarbons and 5 mg/L for methyl-*tert*-butylether (MTBE). MTBE water concentration has been targeted to less than 10 ug/L following local water management specifications. Polluted groundwater was flowed through a sequence of packed beds, each one filled with over 100 kg of Silicalite-1 and siliceous mordenite zeolites, respectively. Most part of the contaminants was adsorbed by Silicalite-1, namely the first zeolite encountered by the water flow. Conversely, siliceous mordenite zeolite took organic molecules too large to enter into Silicalite-1 zeolite pores, completing the removal of all contaminants. This behaviour is exemplified in Fig. 13 regarding MTBE removal.
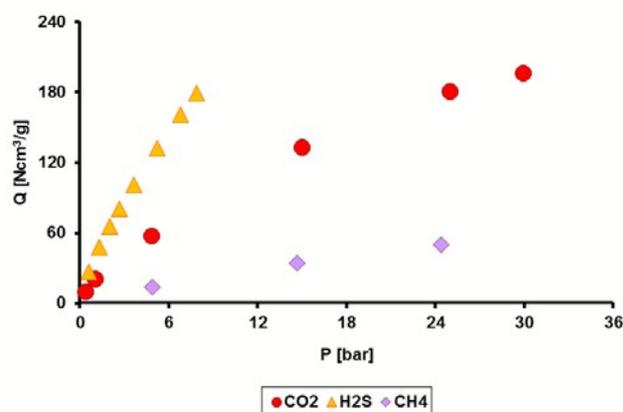

Fig. 12 Adsorption isotherms acquired at 30 °C with pure hydrogen sulphide, carbon dioxide and methane on ERS-8 silica-alumina. [126]
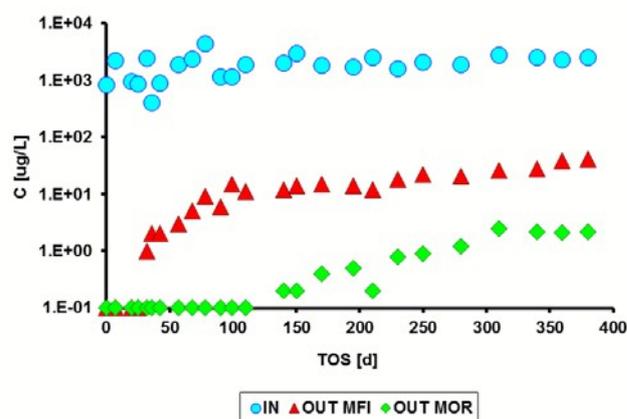

Fig. 13 Implementation of Eni En-Z-LiteTM process for refinery wastewater treatment: MTBE concentration upstream and downstream siliceous zeolite packed beds. (Reprinted from ref. 131, with permission of Elsevier).

Conclusions and perspectives

Over the past decades, the science and technology of zeolites has experienced an impressive growth thanks to the strong interactions between materials science and chemical

engineering. This has had important consequences in the industrial sectors of the petrochemical and oil refining, and have enabled the development of processes that are more efficient and friendly with respect to the environmental issues. In this review, we have summarized the main results we achieved in the synthesis, characterization and application of zeolites and related microporous crystalline materials.

We can consider the experience of Eni as representative of that of the other oil and petrochemical companies, all engaged to exploit the full potential of the crystalline microporous solids in catalytic, separation and adsorption processes. The high industrial interest of these materials has also prompted academia to work in this area, performing the basic research, that industrial laboratories could hardly do, but necessary because it represents the source of knowledge on these complex materials.

As in all other sectors, research activity on zeolites varies according to the technological needs imposed by the evolution of the market and of the regulations. In this regard, it is important to continue to expand the portfolio of materials available to researchers, an indispensable condition to respond effectively to the needs.

The engagement of research on the preparation of new zeolites, led to the impressive number of 231 ordered and 22 disordered (intergrowths of two or more different but structurally related frameworks) zeolite structures officially recognized by the Structure Commission of the International Zeolite Association (SC-IZA). Among them, only around 15 (all discovered in the period 1960 – 1980) have found industrial applications in catalysis, separations, adsorptions and detergency.

In spite of the very recent successes in the preparation of new framework structures with unprecedented porous systems, upon reading these few data one may conclude that the synthesis of new zeolite has reached the technical maturity.

In reality, recent evolutionary developments could open up new horizons. In fact, in the section devoted to the synthesis of the materials, we have stressed the concept that the term "new material" should be understood in a very broad sense, i. e. not limited to a new crystalline structure, but also to all those materials that are derived from the compositional and morphological variation of a known structure. For instance, very recently, the attention of the researchers moved to find the solution of a problem that often cause the rapid deactivation of the zeolite catalysts and, in general, reduce their catalytic performances: the diffusion limitations imposed by the channels.

In this way, interesting approaches aimed at preparing the so-called 2D-zeolites, the nano-sized materials and the materials with hierarchical porosity have recently been developed. The materials obtained by these routes still possess zeolite characters and therefore the peculiar shape-selectivity properties of crystalline microporous solids are preserved. However, the very small dimensions of the zeolite domains reduce in a significant manner the typical drawbacks of the conventional crystals, i.e. consecutive reactions, rapid deactivation due to coking, partial use of the zeolite crystals.

Apart from improving conventional petrochemical and oil refinery processes, the availability of these materials may open new perspectives for the use of zeolites in reactions involving bulky molecules, such as the upgrading of heavy oils and residues and in the conversion of biomasses into biofuels.

Interesting results were recently obtained with the modification of the composition of the framework through the incorporation of organic groups. The research on the synthesis of hybrid organic-inorganic zeolites is still in its infancy, but the results obtained so far indicate that this is a very promising route to prepare multifunctional materials with potential applications in advanced technological fields. These developments bode well for the evolution and the renewal of the zeolites and zeolite-like materials towards new applications of broad interest.

Acknowledgements

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Graphical Abstract

Zeolite science and technology in eni

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This article reviews the results obtained in the synthesis, characterization and applications of zeolites and related microporous materials, focusing on catalytic processes developed in eni research laboratories over the last 40 years.