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Zeolite-based materials for novel catalytic applications: Opportunities, perspectives and open problems

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ABSTRACT

Zeolites and related materials (including a wide range of microporous and mesoporous materials with ordered pore structure) have been one of the areas in the field of materials and catalysis with the largest impact on science, technology and industrial processes. We discuss here some recent developments in this field, with particular references how to tailor and design zeolite and related material properties to control/enhance the catalytic performances. Four main topics have been addressed. (i) The recent progress and perspectives in the field of tailored syntheses, with selected examples showing the trend and prospects to develop new structures, control the location of active sites, and the crystal size and morphology, including nanoarchitecture of the final catalysts. (ii) The development and prospects of two-dimensional zeolites presenting an extended view/concept of zeolite structures integrating the classical 3D frameworks and the various lamellar forms. (iii) The progresses in the design and synthesis of hierarchical zeolites, with discussion on the still existing challenges related to the synthesis, characterization and catalytic application. (iv) Novel opportunities and needs in terms of zeolite multifunctional design for catalytic applications, with a discussion of the critical issues related to the use in the field of fine chemicals, organic industrial syntheses and biorefinery, and the prospects for the use in two novel challenging areas of the direct conversion of CO_2 to light olefins and methane to methanol.

1. Introduction

The area of molecular sieves (micro-porous materials) has been developed in last decades into an impressive group of inorganic-hybrid materials with a huge number of industrial applications, particularly in catalysis. In general, molecular sieves include primarily zeolites/zeotypes [1], mesoporous materials [2,3] and metal-organic-frameworks (MOFs) [4–6] providing unlimited structural and chemical variations [7]. Many of the molecular sieves show interesting properties in adsorption [8], catalysis [9,10], sensing [11], fuel cells [12], medicine or optical applications [13,14], etc. giving rise to a large range of porous materials of high interest [15,16]. The computational advances in this field, integrated with characterization and testing, have provided a remarkably deeper insight to the molecular sieve design [17,18]. Notwithstanding these remarkable advances, the types of zeolites industrially used are still limited to less than 20. There is, thus, the need to consider the opportunities, perspectives and open problems in this field. Coronas [19] and Morris [20] highlighted recently challenges in the synthesis of zeolites and nanoporous materials, but we consider it still necessary to discuss here more practical aspects and examples to illustrate the new emerging trends and the potential for future applications with reference especially to catalysis.

Zeolites represent the most important group of industrial heterogeneous catalysts with large-scale applications in refining and petrochemistry and increasing potential in environmental catalysis and synthesis of fine chemicals [15,21–24]. Zeolites are crystalline microporous aluminosilicates offering a plethora of modifications and opportunities for further improvement of their properties [25]. At present, 200 different structural types have been recognized differing in the size, shape and connectivity of their channels usually being from 8 to 30-rings [26]. The size of zeolite channel entrances sometimes overcomes 1 nm, but it should be stressed that for industrial applications the maximum channel size is still 0.74 nm (12-ring). The possibility to control the textural properties together with adjustable acidity (type, concentration and strength of acid sites) is the most important feature of zeolites [7].

While zeolites are typical three-dimensional (3D) materials, it was recently observed that some zeolites could be formed as layered precursors. The precursors can be further transformed into 3D zeolites via post-synthesis treatment. The understanding of the synthesis mechanism was based on the changes of X-ray powder

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diffraction patterns after synthesis and after calcinations [27–29]. This finding opened new possibilities to tailor the textural features of zeolites. While the first transformations of 2D zeolitic precursors to 3D structures were found accidentally, the synthesis of 2D (lamellar, single-nanosheet) zeolites using designed structure-directing agents by Ryoo and coworkers [30,31] represents real breakthrough in this area with a high application potential.

To overcome the limitation imposed by small channel entrances of zeolites with preservation of their chemical properties, different synthetic approaches have been proposed. One of these is the preparation of so-called hierarchical materials combining micro- and mesoporosity [32–37]. Different synthetic routes were proposed, probably two the most promising include: (i) synthesis of zeolites seeds and their further self-assembly into mesoporous structure and (ii) formation of mesopores in zeolites by direct or post-synthesis ways. Self-assembling methodologies were also proposed to form unique structures [38].

Mesoporous molecular sieves (ordered silica-based mesoporous materials) combine chemical diversity and large surface areas (even higher than 1000 m^2/g) with pores of dimensions between 3 and 30 nm [39–42]. Unfortunately, their walls are mainly amorphous without the presence of strong acid sites (particularly of Brønsted type). Chemical composition of mesoporous materials substantially increased in recent years providing materials like mesoporous carbons, metals, carbide, etc. [43–47]. In addition, structure of amorphous walls has not yet been completely described and strongly depends on the synthesis/calcinations procedures. It results in the formation of “surface roughness” [48,49] and the presence of a corona area in the inner walls and channel-to-channel microporosity [50], which can be suitable, used to develop advanced nanostructured materials for catalytic applications, for example TiO_2@SBA15-like mesoporous nanocomposite [51].

In contrast to different materials based on zeolites or mesoporous molecular sieves being purely inorganic materials, metal-organic-frameworks or periodic-cationic-polymers [52] combine inorganic species bonded via organic linkers forming a three-dimensional crystalline channel system [4]. Metal-organic frameworks offer well-controlled porosity with much larger opportunities with regard to the pore architecture and chemical variety [4]. Nominal surface areas as large as 5000–6000 m^2/g are intriguing properties of some MOFs, however, their lower thermal stability and sometimes even against moisture are considered as weak points. Although MOFs are not yet applied on the industrial scale, some key innovations potentially leading to more economically viable and environmentally friendly processes are expected [53].

In spite of the fact that mesoporous molecular sieves as well as MOFs offer many exciting opportunities as for their adsorption and catalytic properties (mesoporous materials) or chemical and particularly structural features (MOFs), we focus this overview on challenges and perspective of zeolites including hierarchical and lamellar (2D) systems. It was our aim, not only to describe briefly the current status of our knowledge of such materials, but also to highlight and critically discuss the opportunities and perspectives, the open problems to be solved, new areas of application, from environment protection to renewable energy exploitation, etc.

2. New opportunities from tailored syntheses

The perspectives on continuing implementation of zeolite catalysts in several branches of the chemical industries rely basically upon the fine-tuning of the zeolite characteristics to meet those required for the targeted processes. From the point of view of real catalysts, zeolites are much more than just an ideal 3D regular arrangement of TO_4 tetrahedra having channels and cavities that hold appropriate active centers for the incoming guest molecules to react. Zeolite materials are made up of tiny crystals of specific morphologies, always containing defects, sometimes even in abundant amount, and a certain nanoscopic (at unit cell level) and macroscopic (at crystal level) distribution of actives sites, either acid, basic or redox, or a combination of them to make the material even more complex. The scenario would not be complete without mentioning the critical post-synthesis treatments required before zeolite catalysts are put into operation in a chemical plant. Similar considerations would essentially apply as well for zeolite materials used in adsorption processes, although this application would not be covered at length in this brief review.

A survey of publications on the synthesis of zeolite materials in recent years reveals an increasing degree of complexity in the experimental approaches used. For a proper understanding of the available information, it is convenient to classify all these reports under different categories, reducing all of them to a simple question. What can be expected from the synthesis of zeolites? Five different answers have been proposed for classification purposes. First, there is no doubt that the most exciting goal is the crystallization of new zeolite structures. Every new structure is a new possibility of improving an already existing process or dreaming up a new one, after a hard engineering work [54]. Faujasite-based FCC (fluid catalytic cracking) catalysts are still the best example of the radical changes produced by the use of a synthetic zeolite material at industrial scale [55].

Second, new chemical compositions of existing zeolites often open the way to entirely new application fields. TS-1, the Ti-containing all-silica MFI topology material, is a nice example of this aspect [56]. More recently, the successful synthesis of zeolite beta containing tin atoms in tetrahedral coordination has constituted a major achievement in zeolite science [57]. These materials are very active and selective in the activation of carbonyl groups, in particular in the Baeyer–Villiger oxidation of ketones to esters in the presence of hydrogen peroxide and in the reduction of carbonyl compounds to alcohols, the Meerwin–Ponndorf–Verley reaction [58]. Moreover, Sn-beta catalysts have been shown to be active for the transformation of sugars [59,60]. For a given structure and a targeted heteroatom (framework T-atoms other than Si), control of the heteroatom location at the unit-cell scale and at macroscopic scale would be highly desirable, and both could in principle be accessible by an appropriate mastering of the synthesis conditions. Third, siting of T-atoms (site occupancy of crystallographic T sites) and their position within a zeolite crystal is essential for their performance [61,62]. The siting/position is not fixed but depends on the extent of hydration and temperature treatments, because migration from framework to extra-framework position and back is possible. In the fourth place, crystal size and morphology are also critical for many applications, and both depend upon synthesis parameters.

Finally, actual zeolite materials contain a number of defects [63], of various origins, all of which might influence their catalytic performance [64–66]. Let us review in brief the different synthesis approaches used to deal with one or another of these basic objectives, taking into account that often more than just one of these would be affected by changing just one synthesis parameter. Strohmaier [67] has extensively reviewed several of these aspects, while some reflections on challenges for the synthesis of zeolite materials can be found in Refs. [19,20].

2.1. New structures

The use of organic structure directing agents (SDAs) still resides at the core of the efforts to obtain new zeolite structures [68,69]. Not all of them have been equally productive so far in yielding new structures, but we believe they are useful in revealing new aspects of zeolite chemistry, as well as in providing information on research strategies, some of them have been specifically designed to obtain

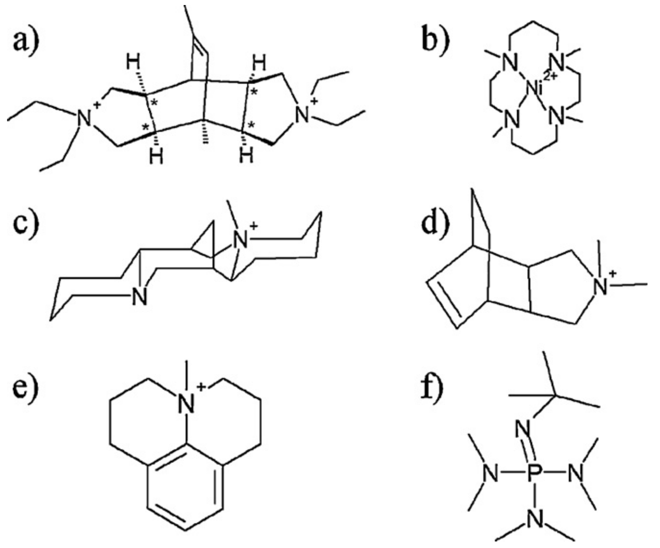

Fig. 1. SDAs used in synthesis of selected zeolite materials. (a) SDA for the synthesis of ITQ-37 (-ITV); (b) Ni-cyclam complex used in the preparation of STA-6 (SAS); (c) N-methyl-(−)-sparteinium for CIT-5 (CFI); (d) 4,4-dimethyl-4-azonia-tricyclo[5.2.2.02,6]undec-8-ene for polymorphs B and C of zeolite beta (BEB and BEC); (e) 4-methyl-2,3,6,7-tetrahydro-1H,5H-pyrido [3.2.1-ij]quinolinium for ITQ-29 (LTA); (f) tert-butylimino-tris(dimethylamino)phosphorane for ITQ-47 (BOG).

large or even extra-large pore materials. In this way, the use of large and relatively rigid SDA, often containing fused 5-and 6-rings, leads to the crystallization of large-pore materials, like SSZ-59, containing 14-ring pores [70], and MCM-68, containing an intersecting 12 × 10 × 10 channel system [71]. Fig. 1 presents as example some typical SDAs used in the synthesis of selected zeolite materials.

Pure all-silica polymorphs B and C of zeolite beta have been also obtained from bulky SDAs [72,73] made from DABCO (1,4-diazabicyclo[2.2.2]octane) derivatives, although the synthesis of the much wanted chiral polymorph A remains still elusive. By using a still larger SDA molecule related to that used to synthesize the beta polymorphs, which contains in addition four chiral centers, the extra-large chiral ITQ-37 germanosilicate with an interrupted framework has been obtained [74]. Even larger SDAs could eventually lead to extra-large pore zeolites, but as their hydrophobicity will increase with their C/N ratio, which would decrease the solubility in water, strategies based on the use of self-assembled SDA molecules have been proposed. The actual SDA in this case is the chemical entity resulting from the aggregation of at least two molecules, being in this way bulkier than the individual molecules, facilitating the eventual templating of large pore materials. Although this strategy does not always result in new large-pore material, it is however interesting to notice that materials containing large voids and/or large pores are indeed obtained. In this way, the self-assembly of two aromatic molecules derived from quinolinium that are held together through π–π-type interactions, allow the crystallization of Al-free ITQ-29 with LTA topology in the presence of Ge, although the pure silica analogue can be obtained if TMA+ cations are used as co-SDA [75]. A similar phenomenon of self-assembling of SDA molecules containing at least one aromatic ring has also been found in a number of AFI-type materials [76].

As chemically complex as they can be, the commonly used SDAs are based on a skeleton of C and N atoms, bonded to H atoms as well. This view has been challenged in a number of ways, which has resulted in some cases in new zeolite topologies. The replacement of the N atom of tetraalkylammonium cations by P atoms gives tetraalkylphosphonium cations. Tetrabutylphosphonium cations were already used for the synthesis of ZSM-11 nearly thirty years ago [77], and the recent use of new phosphonium cations under appropriate synthesis conditions resulted in several new structures, ITQ-40 among them, an extra-large pore material (16 × 15 × 15 tetrahedra forming the ring apertures) containing Si and Ge and D3R and D4R with the lowest known framework density equal to 10.1 [78].

The introduction of phosphazene derivatives has opened very interesting perspectives for the synthesis of new materials, and they have led to the crystallization of synthetic boggsite, containing intersecting 10- and 12-ring channels [79]. Molecules, where F atoms replaced in part the H atoms, have also been used as SDAs [80–82]. As the fluorine-containing molecules are in general more hydrophobic than their all-hydrogen counterparts, the framework–SDA interactions would be affected, and this would eventually led to the crystallization of structures different than those obtained from conventional non fluorinated SDAs. Differences in the crystallization of microporous materials have been found when using these fluorinated SDAs instead of their H analogues.

A key aspect that improved enormously the success in the crystallization of new zeolite structures, many of them of low framework density and large or even extra-large pores, is the simultaneous combination of several synthesis strategies, in such a way that altogether are shown to be very effective in promoting new crystallization pathways. Some structures just mentioned require for their crystallization not only some specific organic SDA, but also the presence of specific heteroatoms, Ge in most cases, although other examples are known where Ga, B, Zn or Be must be present for successful crystallization [67]. Moreover, other components of the synthesis media must be properly adjusted, for instance highly concentrated gels in the presence of fluoride seems to be required in many cases. It is particularly noticeable in this regard that the extremely concentrated gels are needed in many cases, with a water-to-silicon ratios below 4, and even 1 or 2. Such low water content challenges conventional views on zeolite nucleation and growth in diluted systems. In our view, this cooperation between several chemical species present in the synthesis medium is what mostly characterizes the recent advances in the synthesis of new zeolite structures.

2.2. *Location of the active sites*

Development of effective means to control the location of active sites in zeolite frameworks at unit cell scale would have an essential impact in the catalytic properties of these materials. Many zeolites possess a complex architecture of voids and channels, having different dimensions and geometries, offering in this way very different potential reaction environment that would lead to rather specific reaction pathways. In the case of acid sites, the problem is reduced to the control of the location of the aluminum atoms in silica-based zeolites during crystallization. As the presence of aluminum in the framework induces a negative charge in its vicinity, it is commonly thought that it would interact with chemical species bearing a positive charge, i.e., with the inorganic or organic cations (SDA) present in the synthesis medium. In general, the interaction with sodium cations would be nearly nonspecific, in such a way that strategies aiming at controlling the location of aluminum should in principle avoid the use of such small and non-site-sensitive cations.

Based on this premise, a new strategy for controlling the aluminum location in ferrierite structure has been developed using a combination of SDAs of different size, the small one able to direct the formation of the small FER cage, while the large one would only be able to accommodate in the 10-ring channel. It has been shown that by using combinations of different SDAs, it is possible to modify the relative population of acid sites present in the cage that are accessible through 8-ring windows and those present in the 10-ring channel [83–86], for crystals having the same Si/Al ratio. Within certain limits, this strategy could be extended to other structures as well, even in cases where the differences in size between structural elements of the zeolite are not as large as those of ferrierite. Moreover, XRD refinement of the as-made ferrierite revealed that most probably chemical properties of the SDA play also a determining role in its ability to direct the location of Al [87]. On the other hand, this strategy could also be effective with appropriate modifications to control the location of dopant atoms other than Al.

While this strategy would be suitable for controlling the distribution of active sites at unit cell scale, i.e., among the different crystallographic T sites, different methodologies should be developed for influencing the distribution of active sites at macroscopic scale, i.e., across and along the zeolite crystals. This topic has been recently reviewed in Ref. [62]. The control of aluminum distribution throughout zeolite crystals will no doubt have an impact on their catalytic performance. Indeed, we should not forget that the Si/Al ratio of zeolite materials are conventionally used for correlation between aluminum content and catalytic behavior, without considering that this is a bulk value. However, a non-uniform distribution of aluminum over the crystals might exist, which would lead to noticeable differences between samples with the same Si/Al ratio but synthesized with different procedures.

The occurrence of non-uniform aluminum distribution [88,89] is related to the relative nucleation and crystal growth rates, which in turn are influenced by the chemical composition and crystallization temperature of the gel. Aluminum zoning is a time-dependent phenomenon, and it is then not unreasonable to expect that it could be somehow influenced if the synthesis conditions could be modify during the course of the crystallization. As the synthesis of zeolites is carried out nowadays, all components of the gel are mixed at the beginning, and then the resulting mixture is introduced in a suitable container (autoclave) for heating. Once this is done, the system is allowed to crystallize by itself. Would it be possible to alter the system during the crystallization, other than obvious changes in the heating temperature? In other words, could the synthesis mixture be also time-dependent? An efficient *on-line* control of the aluminum distribution in the crystals during the crystallization process would help to a defined design of zeolite materials, especially for catalytic applications.

2.3. Crystal size and morphology

The crystal size, crystal size distribution and crystal morphology are critical issues for catalysis and adsorption. These properties depend on the nucleation and crystal growth steps, and are therefore strongly influenced by the chemical composition of the synthesis gel, crystallization temperature and kinetic aspects [90]. Zeolites with controllable structures and morphologies (sizes and shapes) can be also obtained using polymer networks that function as a space-confinement additive and as a mesopore-forming agent, thus significantly affecting zeolite nucleation and growth processes [91]. Moreover, the relative orientation of the channel system respect to the crystal shape affects the diffusion path of reagents and products through the crystals.

For this reason, efforts have been made to control the shape of zeolite crystals [90]. We will mention here, as examples, only two recent advances in this field. Polytetraalkylammonium cations have been used for the synthesis of silicalite-1 crystals, with the purpose of decreasing the dimension of the crystals perpendicular to the main diffusional path defined by the channel orientation [92,93]. The SDAs used for this purpose contain two or three quaternary nitrogen atoms, linked through a chain of 6 or 7 carbon atoms, and bonded to additional propyl groups. It can be clearly seen in this approach that the structure of the polycation in a way reflects in a single molecule the configuration of the TPA (tetrapropylammonium) cations when they are occluded inside the MFI structure, where the central N atom of the cation resides inside the cavity formed by the intersection of the two channel systems, and the four propyl "arms" bonded to the N atom extend along each of the four channels coming into the cavity. In this way, one propyl group belonging to a given TPA molecule is in close contact with the propyl group of a TPA located in an adjacent cavity. In other words, there are 6 carbon atoms between one N of one TPA and the N atom of the next one.

It is interesting to mention that this approach is closely related to the use of surfactant-terminated polytetraalkylammonium cations, designed to prevent the growing of zeolite crystals perpendicular to the surfactant chain, described in Ref. [31]. This strategy allowed the synthesis of nanosheets of ZSM-5 being 2 nm thick, which corresponds to the dimension of the *b*-axis of the MFI unit cell. In these two approaches there is a close correspondence between structural motifs of the zeolite and geometrical properties of the SDA. There is a big potential for extending this approach to the synthesis of other interesting zeolite materials, which provides a new route toward 2D zeolite materials, complementary to that developed from layered precursors as discussed in the corresponding section of this article.

All these recent approaches for the synthesis of zeolite materials, and several others not mentioned in this brief survey, have an enormous potential to provide new materials for catalytic and adsorption processes, and many of them are currently being explored in this regard.

3. Two-dimensional zeolites

The term 2D zeolites have been adopted recently from the concept of the well-known 2D layered/lamellar solids [94–96], which they resemble structurally, but with the added features of layer porosity and intrinsic catalytic activity [97]. As a phenomenon it has been evolving for about two decades and includes those zeolite materials being composed of layers with approximately one or less unit cell thickness, corresponding to roughly no more than 3 nm, which aggregated in ordered or disordered fashion [97]. These layer assemblies can produce open architecture with enhanced access and mobility of reactants and products [98]. Zeolites have been traditionally found or synthesized in their completed 3D framework form [99,100] as evidenced by the similarity of the unit cell and XRD peak positions between the as-made and final activated calcined crystals.

These fixed structures precluded meaningful non-destructive framework modifications and were viewed as a shortcoming. There was a speculation that zeolite frameworks may require layered intermediates during their formation but the evidence was lacking. A material designated NU-6(1) synthesized with 4,4′-dipyridyl as template having unknown structure did show a profound structural change upon calcination consistent with intercalated layered silicate material [101]. The product, designated NU-6(2) was referred to as zeolite, which it indeed was as shown later [102], but at that time it did not attract much attention.

The breakthrough and a watershed event has been the synthesis of zeolite MCM-22 [103,104]. It was recognized that it did form from as-made layered material designated MCM-22P, having approximately 0.2 nm longer lattice constant in one (layer stacking) direction [105]. It was immediately demonstrated that the layers could be exfoliated before their fusion into a 3D framework (the layers themselves are zeolite crystals with the thickness of one unit cell) [106].

This exfoliation was accomplished by swelling with a cationic surfactant solution and enabled preparation of the first zeolite

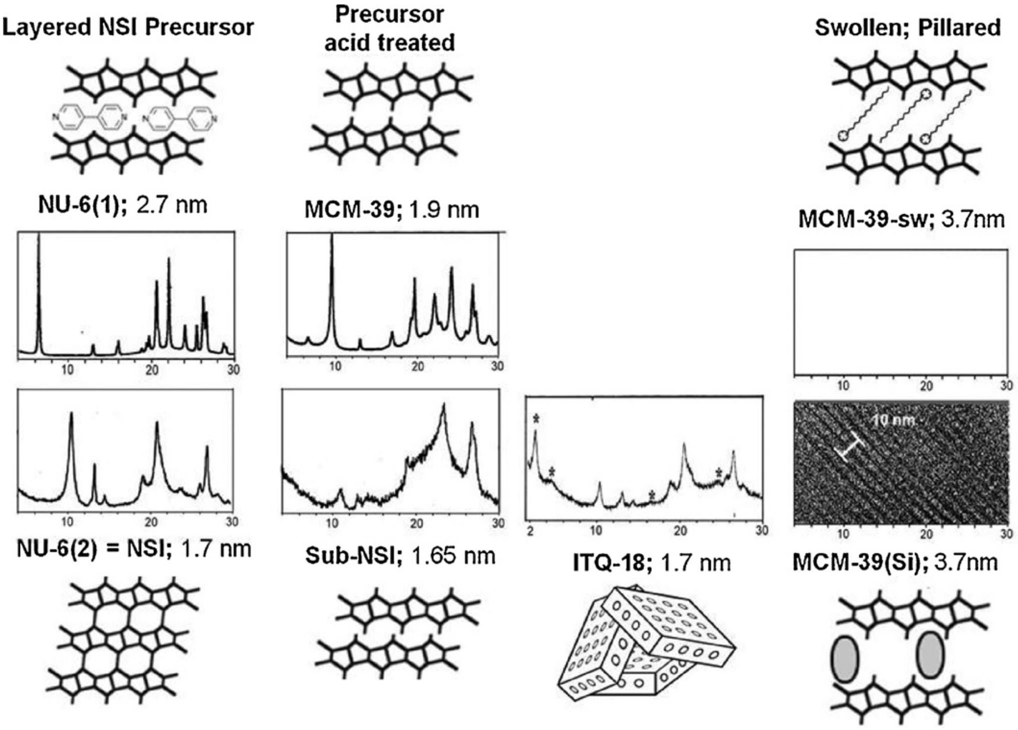

Fig. 2. Zeolite NSI and its known layered forms. The values accompanying labels are approximate interlayer repeat distances (lattice cell constant in stacking direction).

based pillared material, MCM-36 (maybe the first structurally expanded zeolite, too). MCM-36 combines micro- and mesopores with a strong acid activity. In the course of detailed inquiry it was found that MCM-22 framework could form by a direct route as well, i.e. self-assembly in 3D. As an unexpected 'bonus' it was found that there was a layered intermediate in the latter reaction, a single layer, delaminated material designated MCM-56 [107]. Later on, a related delaminated material ITQ-2 was obtained by treatment of the aforementioned swollen MCM-22 precursor [108]. The development of the MCM-22 family of zeolites provided a roadmap for other zeolite materials as their lamellar forms were being discovered [109].

A particularly notable early event was identification of PREFER [110,111], a lamellar form of ferrierite, which is a classical zeolite long time ago recognized in nature. These early findings suggested some fundamental phenomena:

1. Many, maybe all, zeolites can have a lamellar form.
2. 3D zeolite frameworks can be obtained by two (at least) synthetic pathways: direct and via a layered intermediate.

The first decade (1990s) marked a steady but slow progress of layered zeolite materials. New layered precursors were obtained, but exclusively by accident, while characterization and identification of modified products was sometimes not fully substantiated. Several remarkable achievements (*vide supra*) in the recent years justify increased fundamental interest as well as hope in practical expansion.

The first event was referred to as stabilization of the layered precursor, MCM-22P in its expanded form by relatively simple treatment with silylating reactant $Si(CH_3)_2(OC_2H_5)_2$ in nitric acid [112]. It not only did not destroy the zeolite (acid, no Al leaching) but the calcined product was an MCM-22 derivative with effectively 12-ring apertures as opposed to 10-rings if it had been calcined without treatment. Clearly a method of ordered pore enlargement post-synthesis was invented. The second was already mentioned above rational preparation of a single-sheet form of zeolite MFI (ZSM-5) by deliberate design of the structure-directing agent. It is based on the concept of surfactant with a micropore-templating head group [31].

Zeolite MFI has been a versatile commercial success and one of three the most frequently studied zeolites. Its preparation in the 2D form confirmed validity of the concept and the 2D phenomenon as possibly integral part of the zeolite field. The third finding concerns conversion of the 3D framework UTL into previously unknown layered zeolite precursor IPC-1P (the 3D framework still hypothetical) [112,113]. The precursor was subsequently converted into the now standard modifications – stabilized, swollen and pillared. The 3D to 2D conversion was previously reported for Ti-MCM-22, but it did not involve novel layered precursor and was not followed with generation of modified architectures [114,115] The three described inventions are quite unique for zeolites and constitute precedents that may be expanded to other frameworks as is apparently already happening. In the language of Thomas Kuhn regarding scientific and technological progress one can talk about a shift from pre-science to normal science [116].

The increasing scope and diversity of 2D zeolite area led to an extended view/concept of zeolite structures integrating the classical 3D frameworks and the various lamellar forms [27,117]. Most of the latter are not strictly zeolites as lacking 4-connected character in their entirety and therefore are better referred to as *para*-zeolites. At the same time the former, classical 4-connected structures, can be viewed as a special case of 2D zeolites with layers fused congruently with 3D order. This formal concept, in addition to being a classification tool, may be used to establish a protocol for identification and recognition of various structural and other forms. This is illustrated in Fig. 2 presenting various forms of the NSI framework and corresponding X-ray powder diffraction patterns [118,119].

Aside from the formal and fundamental aspects of 2D zeolites, there is the practical catalysis side as they combine the structural flexibility of 2D solids with potential high acid activity and combination with other localized activity of zeolites. As a bridge between these two classes they offer enhanced access to active zeolite sites and potential of activating larger molecules.

Table 1
Known layered precursors with year of preparation or recognition.

Framework (FTC)	Layered precursor designation	Year reported: zeolite, precursor or both
NSI (NU-6(2))	NU-6(1)	1983 (2004[a])
MWW (MCM-22)	MCM-22P	1994
FER	PREFER	1918, 1995
CDO (CDS-1)	PLS-1, MCM-65	2004, 2002
SOD	RUB-15	1811 (1997[b]) 2006
CAS (EU-20b)	EU-19	1980 (1988[b]), 2006
RRO (RUB-41)	RUB-39	2005
RWR (RUB-24)	RUB-18	2004
MFI	Layered MFI	1972, 2009
AFO	PreAFO	1994, 2006
Unknown	IPC-1P (UTL layer)	2011

[a] Structure solved.
[b] Synthesized.

There are many reports and patents demonstrating attractive catalytic activity and improved performance of 2D zeolites compared to the standard 3D forms [97]. In short, there is ample evidence and conceptual justification to consider investigation of 2D as viable candidates for catalytic applications. In most cases, except the delaminated MCM-56, the preparation of a 2D form as an active catalyst requires additional steps, often costly, time consuming and not guaranteeing successful synthesis of the desired catalyst. This, in combination with essentially infinite number of possible structures and compositions to study warrants a judicial choice of materials to study. Table 1 reports the known layered precursors with year of preparation or recognition.

We can think of the following reasons to consider, beneficial, neutral and detrimental, in the investigation of 2D zeolites, in addition to the purely intellectual or 'because it is there' pursuits:

1. In contradistinction to standard zeolites, the ability to modify structure, openness and composition, especially by generation of intimate composites with other oxides, metals, organics, etc.
2. Most likely several-fold increase in cost, labor and effort, which must be in the end offset by the performance or other benefits.
3. Degradation of the layers and or active sites due to treatment or intrinsic reasons because of changed surroundings and external exposure.
4. If a new high performance level is established it may be the target to strive toward with more conventional materials.
5. Most layered precursors to date are highly siliceous and often unattractive for catalytic reactions. The competitors for many such siliceous layered zeolites should be searched among plethora of layered silicates, clays and similar.

As a new area of research, 2D zeolites are wide-open with regard to fundamental issues, new practical opportunities but also daunting challenges. Some of the basic questions are already implicit in the foregoing outline: can all 3D framework be found or made 2D or even of lower dimensionality, what factors determine 2D vs. 3D synthetic routes, and which frameworks can be transformed from 3D to 2D. It is easy to envision that the most elaborate and still unfinished diversity of zeolite MCM-22 can be replicated for the other frameworks (or at least those with known 2D form). The same layer, like FER and NSI, can produce different frameworks depending on how the layers are stacked and in one case it is seen that both options can occur in the same sample [117].

This multiplication of possibilities necessitates focus to future exploration. In view of the successful synthesis by design of 2D ZSM-5 the next obvious candidate is FAU as the second to none in terms of real catalytic applications and potential. MCM-22 lends itself as the zeolite, which is produced by many different templates and producing 4 distinct layer packing by slight changes in synthesis conditions. This is certainly a project worthwhile for close study near term. In adsorption, layered materials when properly modified with aminopropyl groups show a higher efficiency for CO_2 capture than SBA-15 modified by the same amine amount [120].

On the catalysis side one may consider that many catalytic processes by zeolites are quite advanced and the access to real catalysts used commercially is limited. For this reason and others, like economics, it might be more suitable to look for new catalytic process, where the particular character of expanded 2D zeolites may offer advantage compared with standard forms. The concrete example may be a process where a particularly large transition state entity may be involved. Alternatively if rapid desorption is desired the openness of certain forms of 2D zeolites may prove to offer advantage.

4. Hierarchical zeolites

Another alternative to increase the catalytic potential of zeolites is the synthesis of mesoporous analogues of zeolites. Despite the synthesis procedure leading to the mesoporous zeolites (hierarchical zeolites in the sense of having both micro- and mesoporosity), these materials exhibit easier accessibility to acid sites due to the presence of mesopores while the acidity of zeolites is mainly preserved. Generally, two basic methods were described in the literature: (i) direct synthesis, when secondary template (inducing mesoporosity) is added [121–123] and (ii) post-synthesis treatment leading to a partial destruction of the crystals by selective removal of some building units [124–126].

The first approach is usually referred to as "secondary templating method" when a proper template, e.g. carbon black particles, is added to the synthesis mixture together with a template for the synthesis of zeolite, e.g. tetrapropylammonium hydroxide for the synthesis of ZSM-5. When the carbon black pearls (or carbon nanotubes) are properly activated, they can interact with the aluminosilicate species present in the synthesis mixture. As a result, the individual particles are completely covered by the zeolitic structure or are partially buried in the surface layers as was evidenced by 3D TEM images [122]. Calcination then leads to the removal of carbon particles and formation of mesopores inside the crystals as well as to the increase in the external surface. Size of the mesopores (cages inside the crystals) is usually related to the original size of carbon particles. They are accidentally distributed throughout individual crystals, as the reaction mixture is rather dense and optimum distribution in to easily achievable.

In the case of post-synthesis treatments, dealumination (detitanation) or desilication, the removal of individual type of metals depends mainly on the acidity of the treatment solution. While acidic medium is used for dealumination, desilication proceeds easily under basic conditions. Optimum time and conditions are key factors to adjust properly the resulting mesoporosity [35]. While secondary templating method provides relatively uniform pores in size, desilication leads to a broader pore size distribution. This distribution depends on several parameters, namely, type of the zeolite, Si/Al ratio, distribution of Al in the crystals (presence of SiO_2 domains).

There are plenty of examples discussing catalytic behavior of mesoporous zeolites. The reactions investigated include different acid catalyzed reaction but also epoxidations over mesoporous Ti-ZSM-5 or NO decomposition. More specifically, cracking of triisopropylbenzene and some esterification reactions of bulky substrates were catalyzed by hierarchic zeolites prepared using conventional block copolymers [127]. de Jong and coworkers [128] reported high activities of mesoporous mordenite in cumene synthesis. Groen et al. [129] also obtained similar results. Intensive study of mesoporous ZSM-5 provided additional evidence on low *para*-selectivity in *o*-xylene isomerization due to a shortening of diffusion pathways [130]. Production of light olefins in FCC naphtha cracking was reported over mesoporous ZSM-5 catalysts [131]. Desilication of MCM-22 under mild conditions resulted in the increase in accessibility of Lewis acid sites and higher conversion of toluene in its disproportionation while severe treatment led to the destruction of the framework [132].

Catalytic applications of mesoporous zeolites (not depending on the type of mesopores introduction) provide rather consistent picture. The activity of mesoporous zeolites is usually superior to that of conventional zeolites [133–136]. This is mainly due to a faster diffusion of reactants and products based on the presence of mesopores and, thus, an easier accessibility of active sites. It is anticipated that the presence of mesopores decreases the differences in the reaction rates along the individual crystals. While the activity of conventional zeolites is mainly located on the external rim of zeolite crystals, its distribution in mesoporous zeolites is more homogeneous. In addition, selectivity to primary reaction products increases as a result of a shortening of real contact time in mesoporous zeolites. In contrast, selectivity to *para*-isomers in the synthesis of dialkylbenzenes decreases due to a lower contribution of micropores to the diffusion pathways. It can be expected that all reactions related to “product-selectivity” will suffer from this effect. Slower coke formation and prolongation of catalyst lifetime represent a significant advantage of mesoporous zeolites in comparison with conventional ones. Again, it evidences a shortening of the reaction time available for individual product molecules inside the micropores.

Particular challenges related to the synthesis, characterization and catalytic application of mesoporous zeolites include:

1. Synthesis of all known zeolites in the mesoporous form either by direct synthesis or via post-synthesis treatments.
2. Controlled location of active sites (aluminum) in the micropores or mostly on the external surface.
3. Modification of mesoporous zeolites by external functions (e.g. organic groups) to tailor their hydrophobic/hydrophilic properties.
4. Optimization of economy/performance of mesoporous zeolites toward a catalytic application.

Recently, Perez-Ramirez et al. [33] and van Donk and coworkers [133] reviewed different methods leading to hierarchical zeolites according to the principle, versatility, effectiveness, and degree of reality for practical implementation assessing the properties of the resulting materials and their catalytic functioning. Xiao and coworkers [134] reviewed the synthetic routes for preparation of mesoporous zeolites by various templates including nanostructured carbons, mesoscale cationic polymers, mesoscale organosilanes, and nanosized inorganic materials. Christensen and coworkers [36] discussed the use in catalysis of hierarchical zeolites and their future opportunities. Hierarchical zeolites attracted a high interest among the zeolite community, which is nicely recognized by the special issue of Catalysis Today devoted to this topic, some references can be found here [137–141].

5. Needs for novel catalytic applications

Zeolites are the class of catalysts with perhaps the widest range of applications [15,142–144], going from refining to petrochemistry and commodity chemicals, fine chemicals and environmental protection. In addition, zeolites are used in a wide range of different type of reactors and processes, from fixed bed operations in gas phase to fluid- or circulating-bed reactors, slurry processes and even room temperature operations such as in groundwater remediation. To highlight some examples, titanium-silicalite (TS-1) for liquid-phase oxidation processes [56] (propylene epoxidation, hydroxylation of phenols, cyclohexanone ammoxidation [145]; in the latter reaction weak acid and highly defective zeolites such as B-silicalite are used also in the following Beckmann rearrangement step to caprolactam [146]), acid zeolites used in several processes in oil refinery [147] such as fluid catalytic cracking (FCC), hydrocracking, reforming and LCO (light cycle oils) upgrading, olefin oligomerization, and petrochemistry [144] such as alkylation of aromatics (synthesis of ethylbenzene and cumene), alkylaromatic disproportionation and transalkylation, synthesis of dimethylether (DME), methanol to olefins (MTO) and to gasoline (MTG), zeolites containing transition metals used in environmental protection fields [22,148] such as NOx conversion, hydrodehalogenation of halocarbons, and catalytic oxidation of volatile organic compounds (VOC), acid and multifunctional zeolites used in the field of fine chemicals synthesis [149,150] such as Friedel–Crafts acylation and acetylation (anisole, acetylation, synthesis of acetoveratrole, synthesis of hydroxyacetophenones), hydroxyalkylation of aromatics (guaiacol to vanilin alcohol which is easy oxidized to vanilin), Diels–Alder reactions, isomerization (of pinene to limonene), Baeyer–Villiger oxidation, etc.

By the use of zeolites, it has been possible to phase-out several processes based on mineral acids, stoichiometric or toxic/risky reactants, and improve resource efficiency of the processes (lower byproducts and energy consumption) [150,151]. Zeolites are actually used in over 100 industrial processes and the current world production of synthetic zeolites (year 2010) amounts to around 4 million tons annually, for a value of about 3 billion US$. Of the three main areas of applications of synthetic zeolites (detergents, adsorbents/desiccants and catalysis), catalysis accounts for about 20% of the share in terms of volume, but about 50% in terms of revenue.

Microporous acid zeolites (FAU, MOR, MFI, BETA and in minor amount other structures such as FER, LTA, LTL, MTW, CHA, AEL and TON) and bifunctional acid zeolites (containing small mono- or bi-metallic particles) are the most used in industrial applications [54,151], followed at great distance by zeolites containing other transition metals than Al in framework positions (in particular, Ti and more limited Fe) or in some case extra-framework positions (Cu-zeolites). Basic-type zeolites [152] have still limited applications, as well as larger pore zeolites and mesoporous materials. Of the zeotype materials, some silico-alumina-phosphate (SAPO materials, in particular SAPO-34) [153], are also used, but most of the materials developed (micro- and mesoporous materials, and organic–inorganic hybrid materials) have not yet found industrial application as catalysts. Metal complexes hosted inside zeolites or anchored/tethered at mesoporous materials [154,155] have also not find industrial applications, apart for niche cases. The main reasons are still unsatisfactory cost-effectiveness and stability under practical conditions.

There is thus still a discrepancy between the rich variety of materials/characteristics, consequent to the large effort in synthesis and development of micro- and meso-porous materials, and the limited range of materials of industrial use [151]. An area in which a large effort is present to use the increasing knowledge in a tailored design of zeolite and related materials is that of the synthesis of fine chemicals, especially for pharmaceutical, fragrances and agrochemical uses [148,156–158]. Acid zeolites with Brønsted or Lewis acid in carbonium ion reactions as well as metallosilicate (especially, titanosilicate) in oxidation reactions sites have been successfully used in a large variety of organic syntheses. There are a number of advantages, from well-defined isolated sites with tunable acidity to a controlled polarity inside the zeolite, in addition to well-known shape selectivity effects. A limit is still the size of the channels, which slows down diffusion (with negative effect on the reaction rate and deactivation) if not prevents the use with bulky molecules, but fast developments are in progress to develop hierarchical zeolites, nanocrystalline and delamined/nanosheet zeolites, in addition to the development of novel large pores zeolites, as discussed also here. However, often the synthesis of these materials is costly, due to the use of expensive templates or multistep procedures.

This is certain a limitation but the main issue in this field from the application point of view is related to the often low-volume of the target products. This determines the need to use synthesis methods being applicable to classes of reactions [159,160], instead that for a specific substrate, in order to use the same apparatus to produce different chemicals. In addition, each product, even if having a high added value, is synthesized in a total volume, which does not justify the cost of R&D for a dedicated and tailored catalyst. Classical organic syntheses, even if using stoichiometric reactants and having a larger impact on environment, have these characteristics. The main types of heterogeneous catalyst still used in industrial fine chemical synthesis are hydrogenation catalysts, because they also have these characteristics [159]. Thus, in order to foster the use of zeolites and related materials in the field of fine chemicals it is necessary on one side to put more attention on the cost of production of the catalyst and on the other side to develop zeolite and related materials that can be applied to classes of reactions instead of that to specific substrates.

A third component in this picture is the need to change the type of reactors. Continuous-flow reactors versus batch-type reactors offer a number of advantages in terms of lower impact on environment and lower use of resources (energy, solvents, etc.) [161,162]. However, in industrial productions, a minimum volume production for continuous processes is of the order of 5000–10,000 tons per year, which is larger than several of the target fine chemicals. Current reactor and process technologies for continuous operations are not cost-efficient for lower production volumes. It is thus necessary to change technology and go to micro-reactor [163,164] and related technologies (also separation processes should be adapted), which allow process intensification and operate efficiently and in a continuous-mode also for low volume products. However, micro-reactor technology requires also revising catalyst design to develop tailored materials, which can take advantage of the new operating conditions. This area of optimization of zeolite and related material design for the use in micro-reactor and continuous-flow processes for fine chemicals is only starting to be explored [165,166]. There is a need to look more closely at these problems.

A complementary aspect to process intensification is catalyst intensification, i.e. the need to have efficient multifunctional zeolite-based catalysts allowing in one reactor (one-pot synthesis) to realize complex, multistep reactions [54,143]. The reduction in the number of steps, which implies a reduction in the volume of solvent used, number of separation steps, personnel and energy use, etc., is a significant driving force to stimulate the introduction in general of heterogeneous catalysis, and specifically zeolite-type catalysts, in the industrial use for organic and fine chemical syntheses [167,168].

There are many examples in this field, which demonstrates the interest in this area, even though more systematic knowledge is still missing. Boningari et al. [169] reported an interesting example of zeo-click chemistry using copper(I)-zeolite for the one-pot epoxide ring-opening and cycloaddition. Cu^I-USY is an efficient catalyst in multi-component reactions of epoxides with sodium azide and terminal alkynes. Such catalyst allows highly regio- and stereoselective syntheses of hydroxymethylated triazoles. The cascade reaction is made in very mild conditions (water at room temperature). Cu^I ions in the zeolite cages catalyze both the epoxide ring-opening and cycloaddition steps. This cascade reaction was proved to be highly regio- and stereo-selective and tolerated a wide range of functional groups. It is thus an illustrative example not only of cascade reaction, but also of flexible use to a class of products of interest in organic synthesis. Fig. 3 illustrates this "zeo-click" concept [169], in analogy to the "click chemistry" principles developed by Sharpless [170].

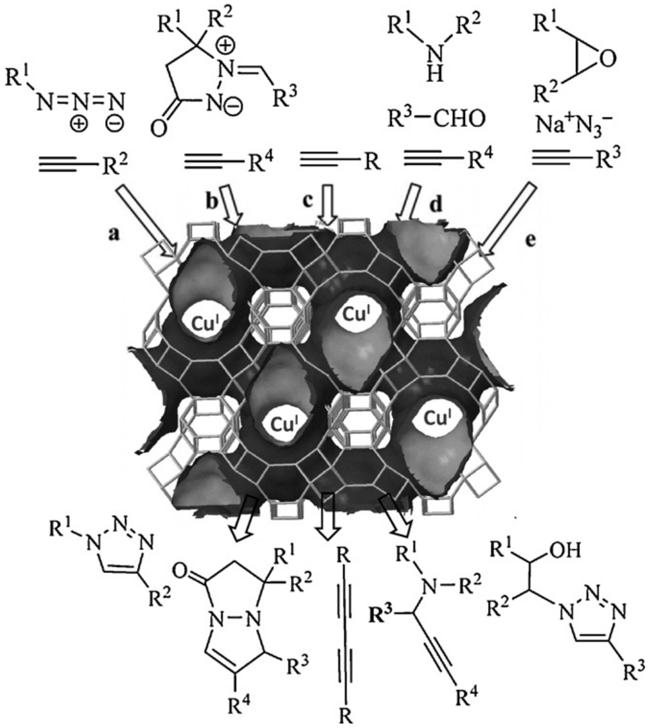

Fig. 3. The zeo-click concept, with Cu^I-zeolites as catalyst. Modified from Ref. [169].

The use of cascade reactions and multifunctional catalysts based on zeolites is also relevant for another area in fast development: the catalytic conversion of biomass to liquid-fuel and/or chemicals [156,171]. The push to shift from 1st to 2nd generation biofuels based on cellulose biomass [172] will make available in the near future large amounts of mono-, di- and trisaccharides from the depolymerization of cellulose. A number of valuable products can be obtained directly from such saccharides [173], to produce polyols or glycerides in one pot, or by transforming these saccharides by dehydration followed by oxidation, hydrogenation, and acid/base-catalyzed reactions [156]. The future for these processes relies on improving multifunctional catalyst properties and tailors their characteristics to operate in aqueous media or biphasic systems with good conversions and selectivities, avoiding multi-step processes that require intermediate separations and purifications [174]. In other words, the ideal solution is to achieve one-pot transformation of cellulose (or at least of the mono-, di- and trisaccharides) into the final products. There is the need to develop specific multifunctional catalysts having the adequate polarity (adsorption properties) and reactant accessibility (porosity), that are efficient in water or biphasic operations with reactants and products of different polarity and size. It evidences great opportunities offered by zeolites and analogous materials from this new field.

Taarning et al. [175] have recently discussed the opportunities for zeolites in the field of biomass conversion with emphasis on the conversion of lignocellulosic material to fuels using conventional zeolites as well as conversion of sugars using Lewis acidic zeolites to produce useful chemicals. Huber and coworkers [176] have instead discussed the role of Lewis and Brønsted acid sites in the design of catalysts for aqueous-phase dehydration of carbohydrates. An interesting example of one-pot synthesis of 5-(hydroxymethyl)furfural (HMF) from carbohydrates using Sn-beta zeolite was reported recently from Davis and coworkers [177]. This Lewis type zeolite shows surprisingly high activities and selectivities for the isomerization of trioses to lactic acid, and for the isomerization–esterification to form lactate esters [178].

There is a series of interesting examples showing how the combination of Lewis and Brønsted acidity in zeolites allows optimizing the performances in producing chemicals from biomass transformation. One example is provided by Corma and coworkers [179] reporting on the etherification of HMF into 5,5′-(oxy-bis(methylene))bis-2-furfural (OBMF), which is an interesting prepolymer and antiviral precursor. Lanzafame et al. [180] examined the role of Lewis and defect sites in zeolites and mesoporous materials for the etherification of HMF with ethanol to form different products of interest as biofuels: 5-(ethoxymethyl)furan-2-carbaldehyde (EMF), 1,1-dietoxy ethane (DE) and ethyl 4-oxopentanoate (EOP). Depending on the nature and strength of the acid sites a drastic change in the selectivity to these products could be obtained, but the synthesis of EMF, a valuable biodiesel component, requires very weak acid sites, associated to defect sites, in combination with Lewis acid sites.

While refinery application for zeolites is essentially dominated by the reactivity associated to strong Brønsted acid sites [147], these examples for biorefinery show that other type of sites (Lewis acid sites, defect sites, etc.) are those playing an important role, being most of the reactions of interest closer to fine chemical synthesis, both in terms of type of molecules and reactions, and in terms of reaction conditions.

We have not discussed the use of base zeolites [181,182], which are important for example in the production of 1st generation biodiesel by transesterification [183]. However, also in 2nd generation biofuel production, a number of reactions of interest (for example, aldol condensation) involve basic sites. de Jong and coworkers [184] reported that C5–C6 sugars could be converted into C7–C15 hydrocarbons by a sequence of reactions: acid dehydration of carbohydrates giving furfurals (such as HMF) which were coupled by aldol condensation over solid base catalysts, and the resulting molecules are then converted into alkanes via dehydration/hydrogenation over bifunctional catalysts. Engine tests with these alkanes gave excellent results, and the used fuels were superior in quality and more cost efficient than other biofuels for the substitution of mineral oil based fuels. While this sequence of reactions could be realized in different reactors with different catalysts, the challenge is clearly the development of a single multifunctional catalyst able to make in a single reaction this complex chemistry, because otherwise the production of 2nd generation biofuel via catalytic routes will be not competitive.

Dumesic and coworkers [185] proposed the conversion of γ-valerolactone (GVL, produced by hydrogenation of levulinic acid via acid catalysis from agricultural waste through the intermediate formation of HMF) as a potential commercial process to produce liquid alkenes for transportation fuels. The GVL undergoes decarboxylation at elevated pressures (e.g., 36 bar) over an acid catalyst to produce a gas stream composed of equimolar amounts of butene and carbon dioxide. This stream is fed directly to an oligomerization reactor containing an acid catalyst (e.g., H ZSM-5), which couples butene monomers to form condensable alkenes with molecular weights that can be targeted for gasoline and/or jet fuel applications. Also in this case, there is a need to reduce the complexity of the process and the number of steps using a multifunctional catalyst. An increasing attention is given recently to the use of HMF as platform molecule in biorefineries, especially for agrodistricts [180,186]. The key aspect is the use of a molecule deriving from sugars, but without loss of carbon atoms, i.e. preserving intrinsic energy, which can be flexibly converted to either chemicals or biofuels. This requires a new catalytic (multifunctional) chemistry and zeolites and related materials (including mesoporous ones) offer the advantage of an established knowledge on tailored synthesis in terms of pore and crystal engineering, presence of different active acid and redox sites and control of the hydrophilic character, another critical parameter often not considered.

There are many other novel challenges for zeolites related to new areas of development for catalysis. Another interesting example regards the valorization of CO_2. The conversion of CO_2 to fuels and chemicals is a valuable possibility to exploit a low-cost (even negative value) raw material and to reduce the impact on the environment [187]. One of the emerging possibilities is the reuse of carbon dioxide to produce olefins in substitution/integration to the current energy-intensive methodologies starting from oil, or via syngas from other fossil fuel resources, when hydrogen from renewable resources could be available at competitive costs [188]. The mechanism of reaction involves a first step of reverse water gas shift (rWGS) to produce a $CO/CO_2/H_2$ ($+H_2O$) mixture which may be either converted to light alkenes (C2–C4) over modified Fischer–Tropsch catalysts or to methanol further directly converted to light olefins as in MTO approach. Also in this case, the challenge is to perform all these reactions in a single step over a single composite catalyst containing narrow-pore zeolite. Catalyst design is particularly relevant in this case.

Jiang et al. [189] used zeolite capsule catalyst with a core (Fe/SiO_2)–shell (silicalite-1) structure for the direct synthesis of light alkenes from syngas. This zeolite capsule catalyst exhibited excellent selectivities compared with the traditional FT catalyst, suppressing formation of the undesired long-chain hydrocarbons. The next step is to introduce catalyst functionalities for direct synthesis of light alkenes from CO_2/H_2. An issue in reverse-water–gas-shift reaction (rWGS) is the formation of water, which negatively influences the FT synthesis, besides to limit conversion, being rWGS a reversible reaction. However, it is possible to combine the above catalysts with zeolite-based water permeoselective membranes to improve the performances [190]. This area of the development of zeolite-based catalytic membranes is an area exhibiting fast development and is promising from the application perspective [191–193], even if there is still a mismatch between rate of catalytic reaction and permeability rate.

The alternative approach is based on the combination of catalysts for rWGS and methanol reaction with zeolites able to convert the methanol to light olefins. Kang et al. [194] used Fe–Cu–K catalysts supported on ZSM-5 to improve the selective olefin production. Fe–Cu–K/ZSM-5 catalyst with a low Si/Al ratio (25) is superior to the other catalysts in terms of better C2–C4 selectivity and higher olefin/(olefin + paraffin) ratio. Park et al. [195] used instead a dual-bed reactor approach, with a Fe–Cu–Al catalyst in the first stage and a ZSM-5 catalyst in the second stage. Doping with K the first catalyst enhances the formation of olefins. 52% selectivity to C2–C4 hydrocarbon rich in olefins (77% selectivity) was reported. Note that in MTO process small pore CHA-type zeolites such as SAPO-34 are used instead of medium pore MFI zeolite as in the former cases. In addition, a proper catalyst design, such as the use of core–shell nanocomposite would be better. There is thus still significant space to improve these preliminary results and design more effective, multifunctional catalysts for the direct conversion of CO_2 to light olefins.

Another great challenge and still a holy grail is the direct methane to methanol conversion using solid catalysts, but significant progresses in this area have been made recently using Cu-zeolites. Schoonheydt et al. [196] published recently a review on transition-metal ions in zeolites, in relation in particular to the coordination and activation of oxygen. Earlier findings in this field

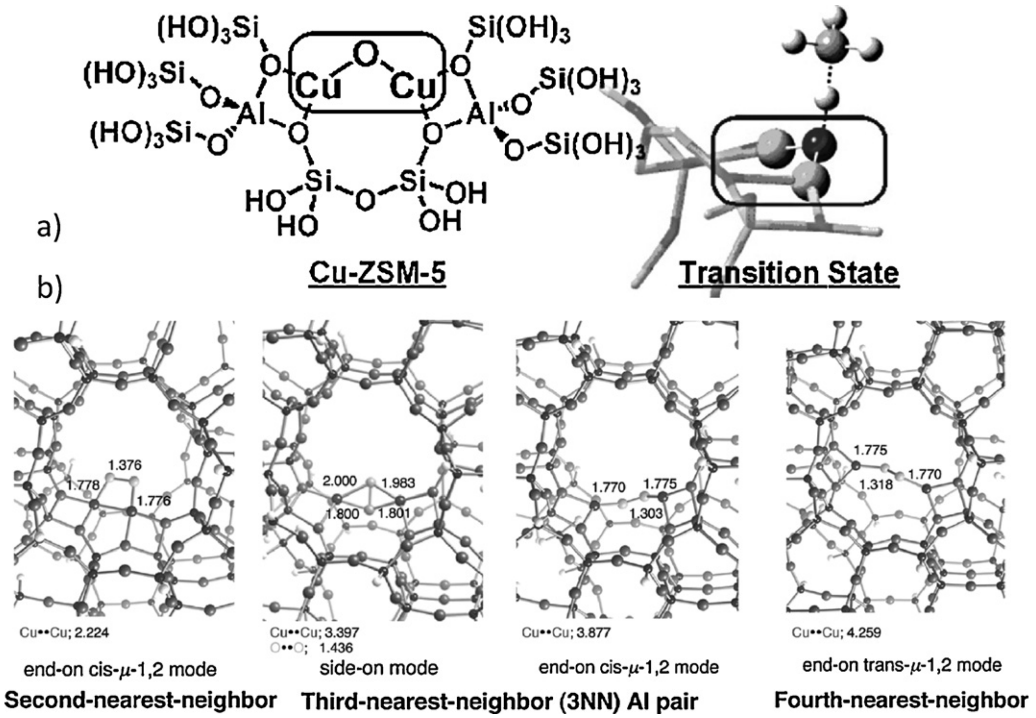

Fig. 4. (a) Hypothetical methane-oxidizing copper-oxy species: the Cu-ZSM-5 active site model and C–H abstraction transition state. (b) Local structures of four optimized $O_2\cdots Cu_2$ complexes where dioxygen binds into the two Cu cations enclosed in $Al_2Si_{90}O_{151}H_{66}$ clusters. The four types of optimized structures can be distinguished by the positions of the double Si → Al substitution: the two substituted Al atoms are in second nearest-neighbor (2NN), third-nearest-neighbor (3NN), and fourth-nearest-neighbor (4NN) positions in a 10-membered ring.

(a) Adapted from Refs. [204,207]. (b) Adapted from Ref. [208].

have been instead discussed in the book “Catalysis by Unique Metal Ion Structures in Solid Matrices” [23].

Zeolites containing transition-metal ions (particularly, Cu, Co, and Fe) have been known from long time. Between the applications, we may cite the conversion of NOx in autoexhaust emissions (using ammonia or hydrocarbons are reductants) [197], the decomposition of NO or N_2O [198], and the selective hydroxylation of benzene to phenol using N_2O as oxidant [199,200]. None of them, however, gained practical application, except for the decomposition of N_2O or catalytic reduction of N_2O with hydrocarbons [201], for various reasons from insufficient stability to low activity. In general, at low loading, transition-metal ions (TMI) preferably occupy exchangeable sites in six-oxygen rings (6R), where the TMIs preferentially coordinate with the O atoms of Al tetrahedra. At least three exchange sites can be identified in zeolites, denoted as α, β, and γ sites [201–203].

High TMI loadings result in a variety of TMI species formed at the zeolite surface. Removal of the extra-framework oxygen atoms during high-temperature pretreatments can result in autoreduction. Oxidation of reduced TMI sites is often accompanied by the formation of highly reactive oxygen species. In Cu-ZSM-5, calcination with O_2 results in the formation of a species, which was found to be a crucial intermediate in both the direct decomposition of NO and N_2O and the selective oxidation of methane into methanol.

Recently, the active site in Cu-ZSM-5 was identified as a bent $[Cu–O–Cu]^{2+}$ core [204], following the earlier communications [205,206] reporting the capability of the O_2-activated Cu-ZSM-5 and Cu-MOR zeolites to selectively convert methane into methanol at a temperature of 398 K. A strong correlation between (i) the activity and (ii) the intensity of the 22,700 cm^{-1} UV–vis band, assigned to the bis(μ-oxo)dicopper core, was found (i) as a function of the reaction temperature, (ii) as a function of the Cu loading of the zeolite, and (iii) in comparison to other Cu materials. In the following work [204] this absorption band at 22,700 cm^{-1} was used to induce the selective resonance Raman vibrations. $^{18}O_2$ labeling experiments allow definitive assignment of the observed vibrations and exclude all previously characterized copper–oxygen species for the active site. In combination with DFT and normal coordinate analysis calculations, the oxygen activated Cu core is uniquely defined as a bent mono-(μ-oxo)dicupric site. Spectroscopic validation of electronic structure calculations shows polarization of the low-lying singly occupied molecular orbital of the $[Cu_2O]^{2+}$ core, which is directed into the zeolite channel, upon approach of CH_4. This induces significant oxyl character into the bridging O atom leading to a low transition state energy consistent with experiment and explains why the bent mono-(μ-oxo)dicupric core is highly activated for H atom abstraction from CH_4. Fig. 4a reports the proposed Cu-ZSM-5 active site model and C–H abstraction transition state.

Several variants of oxidatively capable $Cu_x–O_y(H)$ complexes have been characterized spectroscopically and/or structurally in discrete inorganic complexes [207], but yet none of them showed the capacity to oxidize CH_4. What makes the Cu-ZSM-5 site so reactive toward C–H bonds? A further aspect to consider is that quantitative estimations indicate that only around 5% of the copper sites (which are already low; the copper loading is 1–2 wt.%) are those active. It is thus difficult to really demonstrate that the sites identified as present are those also active in the reaction.

Density functional theory (DFT) calculations to examine the energetics of the dioxygen intermediates inside a 10-ring of Cu-ZSM-5 showed that the properties of the $O_2\cdots Cu_2$ complexes [208], such as the O_2 bridging modes and O_2 activation, are strongly affected by the locations of the two Al atoms within the 10-ring. In particular, the $O_2\cdots Cu_2$ complexes have either end-on or side-on bridging modes depending on the substituted Al positions (Fig. 4b). On the other hand, the steric hindrances of a ZSM-5 cavity determines the properties of the bis(μ-oxo)dicopper complexes containing a diamond Cu_2O_2 core. By restricting its Cu_2O_2 core to a 10-ring of ZSM-5 in which the two Al atoms are

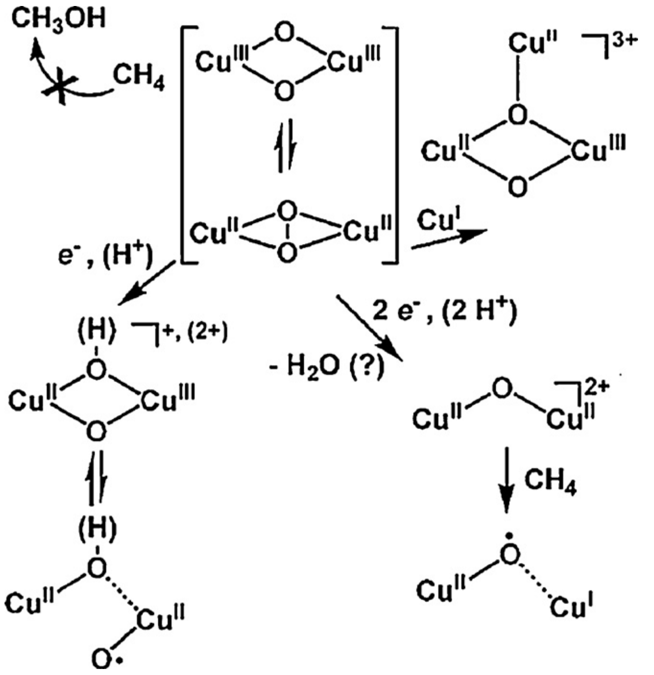

Fig. 5. Proposed evolution of methane-oxidizing Cu–O cores by reduction of species inert toward alkane C–H.
Adapted from Ref. [207].

second-nearest neighbors, each Cu cation is tetrahedral four-coordinate. On the other hand, the Cu cations have almost square planar coordination inside ZSM-5 where the Al atoms are the fourth-nearest neighbors.

The different Cu coordination environments are responsible for the different levels of stability. The planar diamond Cu_2O_2 core is about 31 kcal/mol more stable with respect to the tetrahedral case. Since the ZSM-5 nanospaces directly influence the stability of the bis(μ-oxo)dicopper complexes by changing the Cu coordination environments, zeolite confinement effects on the bis(μ-oxo)dicopper complexes are more noticeable than those in the $O_2 \cdots Cu_2$ cases. This also indicates that the spatial constraint from the ZSM-5 should significantly contribute to the stability of the reaction intermediates formed during the dioxygen activation. Kuroda and coworkers [208], studying the C–H activation of CH_4 in CuMFI zeolite, showed that there is a specific interaction between Cu^+ in MFI and CH_4, even at temperatures around 300 K. However, single copper ions have been only considered.

As shown in Fig. 5, the di-copper sites may further transform to copper-oxyl (radical), i.e., "cupryl" character, the species described by Kuroda and coworkers [209] and other authors [210,211] to have high reactivity toward C–H bonds. However, as shown in Fig. 5, the presence of even more complex situations, with 3 or more copper ions being involved in the active sites, is possible [211].

It is still not conclusively clarified why the active sites in Cu-ZSM-5 catalysts selectively oxidize methane to methanol, neither what is the nature of the reaction cycle. Remarkable, however, is the analogy with enzymes (methane monooxygenase), which are able to oxidize CH_4 to CH_3OH at room temperature and under atmospheric pressure [212,213]. It is not the place here to discuss in-depth the nature of the active centers in Cu-zeolites able to selectively convert methane to methanol but should be evidenced how these frontier studies put in perspective the possibility to create inside zeolites unique structures for multinuclear transition metal centers with peculiar catalytic reactivity.

From the application point of view, the issues of Cu-ZSM-5 methane oxidation to methanol are the need to operate at different temperatures to complete the cycle and especially the low productivity. As discussed also in this contribution, there are new methods to control by synthesis the location of Al pairs, at least partially, but this method has still not be applied to control the nature and structure of transition metal ions in zeolites. There is possibility to tune these materials and optimize their performances to develop novel industrial catalysts for this challenging reaction of direct methane transformation to methanol, which can open new frontiers in sustainable energy and chemistry.

6. Conclusions

Zeolites and related materials (including a wide range of microporous and mesoporous solids with ordered pore structure) exhibit the largest impact on science, technology and industrial processes in the field of materials and catalysis. While known for a long time, it is only in the last 50 years that the science and technology of these materials has been dramatically progressed. It is surprising how today, after so many years of investigation, still new breakthroughs continue in the synthesis and application of these materials.

We have discussed herein some recent developments in the field of zeolites, with particular reference to how to tailor and design zeolite and related materials properties to control/enhance the catalytic performances, with selected examples that highlight and critically discuss the opportunities and perspectives. We also discuss the open problems to solve, for new areas of application, from environment protection to renewable energy exploitation.

Tailored syntheses still offer the possibility of fine-tuning zeolite characteristics to meet those required for the targeted processes, as well as to develop new structures. Selected examples showed the trend and prospects to develop new structures, control the location of active sites, as well as the crystal size and morphology, including nanoarchitecture, of the final catalysts.

Two-dimensional zeolites are another fast growing area offering new opportunities to develop high surface area materials avoiding mass transfer limitations. The increasing scope and diversity of 2D zeolite area led to an extended view/concept of zeolite structures integrating the classical 3D frameworks and the proliferating lamellar forms.

Hierarchical structures are still another alternative increasing the catalytic potential of zeolites. Despite more elaborated synthesis procedures leading to the mesoporous zeolites (hierarchical zeolites in the sense of having both micro- and mesoporosity), these materials exhibit easier accessibility to acid sites due to the presence of mesopores while the acidity of zeolites is mainly preserved. However, while the detailed studies in this area are increasing, still many challenges related to the synthesis, characterization and catalytic application exist.

Also in terms of catalytic applications, new challenges are presented by the use to the field of fine chemicals and organic industrial syntheses, but it is evident how the critical issues are to develop, on the one hand, multifunctional catalysts able to accomplish in one-step some complex multistep reactions and be able to operate as well with bulky molecules, and on the other hand to implement these new catalysts in novel microreactors to operate in a continuous-flow mode even for relatively small industrial productions.

The development of bio-refinery processes also requires novel multifunctional zeolites. A series of examples are presented showing how different zeolite functional properties, with respect to those used in refinery processes, are necessary. Two further challenges related to the use of zeolite-based materials for the direct conversion of CO_2 to light olefins and methane to methanol are presented to give a glimpse of new areas of development.

In conclusion, the only limitations in zeolite research are in our imagination [15], but this field of research is still able to excite researchers and provide new solutions for the demanding new societal challenges in terms of clean energy, sustainable processes and environment protection.

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