

Habilitační práce
Rozvoj pokročilých porézních materiálů
(Design of advanced porous materials)

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Design of advanced porous materials

Introduction

Microporous, mesoporous and combined micro-mesoporous molecular sieves are a key group of materials with a wide range of applications in catalysis, adsorption, separation, sensing and other fields. Among these compounds, zeolites and metal-organic-frameworks (MOFs) stand out as microporous representatives of this group for their wide use in the industry or high potential for such purposes in the near future. Hierarchical (micro-mesoporous) zeolites provide even more advantages by facilitating diffusion and increasing reaction space in comparison with conventional, purely microporous solids. Accordingly, the synthesis, characterization and use of these materials is a constantly growing field, particularly thanks to the invention of modern synthesis strategies and to development of sophisticated analytical techniques, which enable fine tuning and controlling properties such as framework structure, nature and localization of catalytically active sites, state of active species and confinement features. Considering the importance of the design and application of crystalline molecular sieves, over the past 7 years, I have focused my scientific interest on the following sub-topics, which will be addressed in separated chapters below:

- Design of hierarchical, two-dimensional and novel tree-dimensional zeolites;
- Adjustment of the properties of zeolites using post-synthesis top-down approaches;
- Development of hybrid organic-inorganic solids with tunable textural properties;
- Application of metal-organic frameworks as catalysts in liquid phase reactions.

Design of hierarchical and two-dimensional zeolites for catalytic applications

(Representative publications on this topic: *Chem. Soc. Rev.* 44 (2015) 7177–7206; *Angew. Chem. Int. Ed.* 56 (2017) 4324–4327; *ACS Catal.* (2015) 5 (4) 2596–2604)

Notwithstanding the long history and understanding the chemistry of zeolites and their catalytic behavior, both traditional and emerging fields of applications (e.g. optics, electronics, energy storage) still face many problems, which cannot be solved using traditional, or tree-dimensional (3D), zeolite materials. For example, poor transport pore interconnectivity and slow molecular transfer in pore systems can be partly overcome utilizing hierarchical materials. In addition, one of the most demanding subjects, which remains topical despite the numerous approaches currently available for design of hierarchical materials, is the precise adjustment of zeolite structures at the nm-scale, which is extremely difficult to control. Nevertheless, these issues can be overcome by generating two-dimensional zeolites (known as layered, nanosheet, or 2D zeolites) with layer thickness typically ranging from a few nanometers to dozens of nanometers (*Adv. Mater.*

2018¹). Over 20 years ago, the first zeolite with an MWW topology was synthesized via topotactic condensation of the respective layered precursor consisting of regularly stacked lamellas of unit-cell thickness (*Leonowicz et al. Science 1994, 264, 1910*). Since the zeolite layer can be considered the 2D building block, this discovery stimulated numerous studies on the manipulation of zeolites through the organization of layer assemblies (Fig. 1).

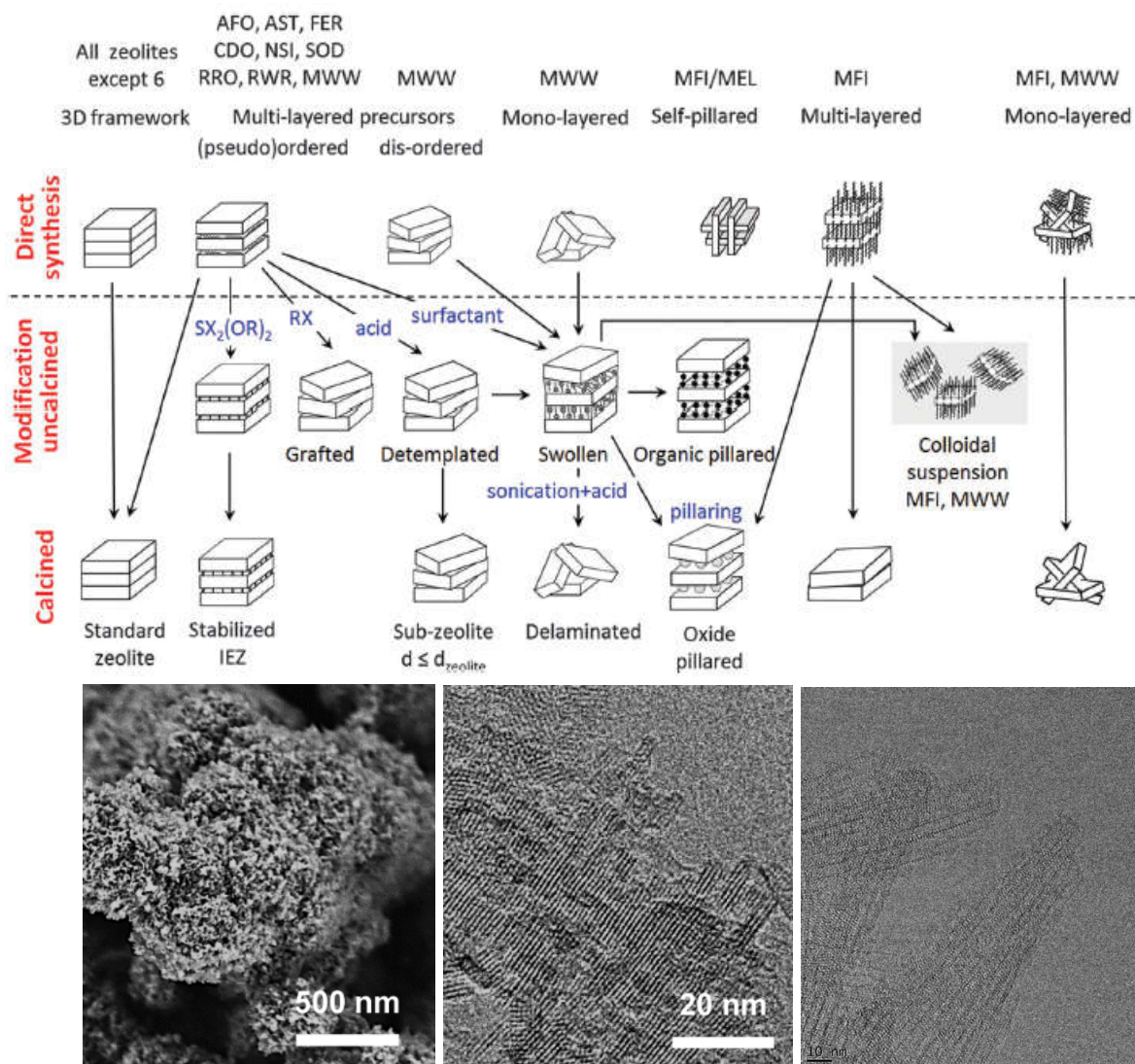


Fig. 1. top – preparation routes and principal pathways for the modification of 2D layered zeolite materials (from *Comprehensive supramolecular chemistry II 2017*); bottom – examples of TEM images of 2D and hierarchical materials prepared by direct bottom-up synthesis: left and middle – nanosponge MFI zeolites (*ACS Catal. 2015*), right – lamellar MFI (*ChemCatChem 2014*, scale bar is 10 nm).

¹ Citations with M. Opanasenko as a co-author are presented as {Journal Name + Year} due to the commentary size limitation. Full description can be found in "Bibliography" attachment. The rest of citations contain full information.

Interlayer distances can be changed when assembling layers by swelling and pillaring using various inorganic or organic props, with a high potential for further exfoliation (*Dalton Trans.* 2014). In addition, 2D zeolites (and hence their assemblies with hierarchical porosity) can be synthesized using either bottom-up or top-down strategies. Bottom-up methods range from hydrothermal synthesis, wherein adjusting reaction conditions usually leads to conventional 3D zeolites, to synthesis with special structure-directing agents (SDAs). In turn, the top-down method is based on the disassembly of previously prepared zeolites. The 2D zeolites prepared using these methods can be subsequently used i) as catalysts and membranes after exfoliation or ii) as relatively bulk building units to prepare pillared materials with organic or inorganic props or to synthesize new zeolites.

The majority of known 2D zeolites are intermediates (layered precursors) formed during conventional hydrothermal syntheses using low-molecular weight SDAs. Alternative method based on spatial structure directing phenomena has been developed for the preparation of the layered zeolite with MFI topology (*Choi et al. Nature* 2009, 461, 246). The rationale of this approach consists of using multifunctional cationic SDAs consisting of two fragments: one responsible for the crystallization of the zeolite phase, while the second part prevents the formation of 3D material. These bifunctional SDAs possess i) quaternary ammonium (e.g. $-\text{N}^+(\text{CH}_3)_2-$) groups allowing zeolitization and ii) a hydrophobic long aliphatic chains fragment (e.g. $\text{C}_{22}\text{H}_{45}-$) preventing the condensation towards 3D structure. Both moieties of multifunctional SDA molecules (hydrophilic and hydrophobic) can be adjusted to tune the structure of the derived lamellar material. The SDA used to prepare a specific 2D zeolite is still situated in the pores after the synthesis, while the distance between layers in the final material depends on the size of the aliphatic chain in the SDA molecule. Varying the number of $-\text{N}^+(\text{CH}_3)_2-$ groups connected through aliphatic linkages makes it possible to control the thickness of the resulting layers. Lastly, by changing the nature of the N-atom environment (e.g., utilizing Ar groups instead of Alk), the crystallization process can be further tuned to design mesostructured zeolite nanosheets or intergrown layer assemblies. Similarly, the synthesis conditions can be adjusted to change the layers arrangement, thereby preparing multilayered and single-sheet assemblies of MFI nanolayers with different degree of the order (Fig. 1).

In contrast to single-chain multiammonium surfactants, gemini-type SDAs with formula $[\text{C}_n\text{H}_{2n+1}-(\text{N}^+(\text{R})_2-\text{C}_6\text{H}_{12})_m-\text{N}^+(\text{CH}_3)_2-\text{C}_n\text{H}_{2n+1}]$ ($n = 16 - 22$; $m = 2, 3$) can be used to produce zeolite layers of nm thickness and regular order. These surfactants make it possible to fine-tune both the thickness of zeolitic walls and spatial arrangement of mesopores by the selection of appropriate amphiphilic SDA. In this context, the catalytic behavior of aluminosilicate MFI nanosheets with different wall thickness (from 1.7 to 2.7 nm) and order was examined in the cyclization reaction using substrates of different kinetic diameter: phenol (kinetic diameter = 0.66 nm), 1-naphthol (0.80 nm), and 2-naphthol (0.89

nm) (*ChemCatChem* 2014), showing the higher activity of these nanolayered zeolites over bulk ZSM-5 for all phenols. Particularly for the large 2-naphtol, the conversion over 3D and 2D catalysts totaled 0 % and 55 %, respectively. Overall, the performance of MFI nanosheets increases with the decrease in layer thickness, i.e., with the increase in surface area of the study material.

The top-down approach for 2D zeolite design is grounded on the selective chemical transformation of a previously synthesized 3D zeolite to its 2D form taking advantage of the anisotropy in the one-dimensional crystal structure. To enable the further rearrangement, the layers of starting zeolite must remain unaffected throughout the process. Only then the disassembly of a fully condensed zeolite will result in the respective layered derivative (*Chem. Soc. Rev* 2015). Furthermore, a top-down transformation requires the selective positioning of chemically unstable units between lamellas. Both aforementioned conditions can be implemented using, as parent zeolites, germanosilicates consisting of Si-enriched layers propped by Ge-enriched double-four ring (D4R) building units. When the Si/Ge in the layers is high, the structure of layers remains unchanged throughout the treatment. In contrast, a low Si/Ge in D4Rs offers the necessary lability and enables the disassembly or reorganization of the respective units. The mild and chemo-selective fragmentation of germanosilicates with different topologies, such as UTL, IWR, ITH, ITR (*Chem. Mater.* 2014), makes it possible to remove Ge-rich D4Rs, thereby producing 2D materials whose layers have a structure related to that of their parent zeolites.

Unlike several other materials prepared by direct synthesis, the top-down method allows the preparation of layers with < 1 unit cell thickness, which is a potential advantage. However, the small thickness (and porosity of some layers) destabilizes the corresponding two-dimensional zeolite layers, thereby limiting their applicability for post-synthesis transformations. For example, swelling and exfoliation must be avoided considering the severe conditions that are typically applied during these procedures. Another issue restricting the swelling and delamination of layered zeolites prepared by top-down methods is the high concentration of OH groups formed on the surface during layer disassembly because strong H-bond interactions limit the layers ability to move apart.

Rather than directly using layered materials, such 2D products can be utilized as bulky building blocks for organization (systematic arrangement of layer ensembles) and then reassembly (topotactic condensation) of the lamellas into 3D zeolites. This reassembly makes it possible to synthesize new zeolites previously unattainable by direct hydrothermal approach (*Angew. Chem. Int. Ed.* 2014). The overall approach of considered multistep transformation is developed as ADOR (Fig. 2) – Assembly-Disassembly-Organization-Reassembly (*Chem. Soc. Rev* 2015).

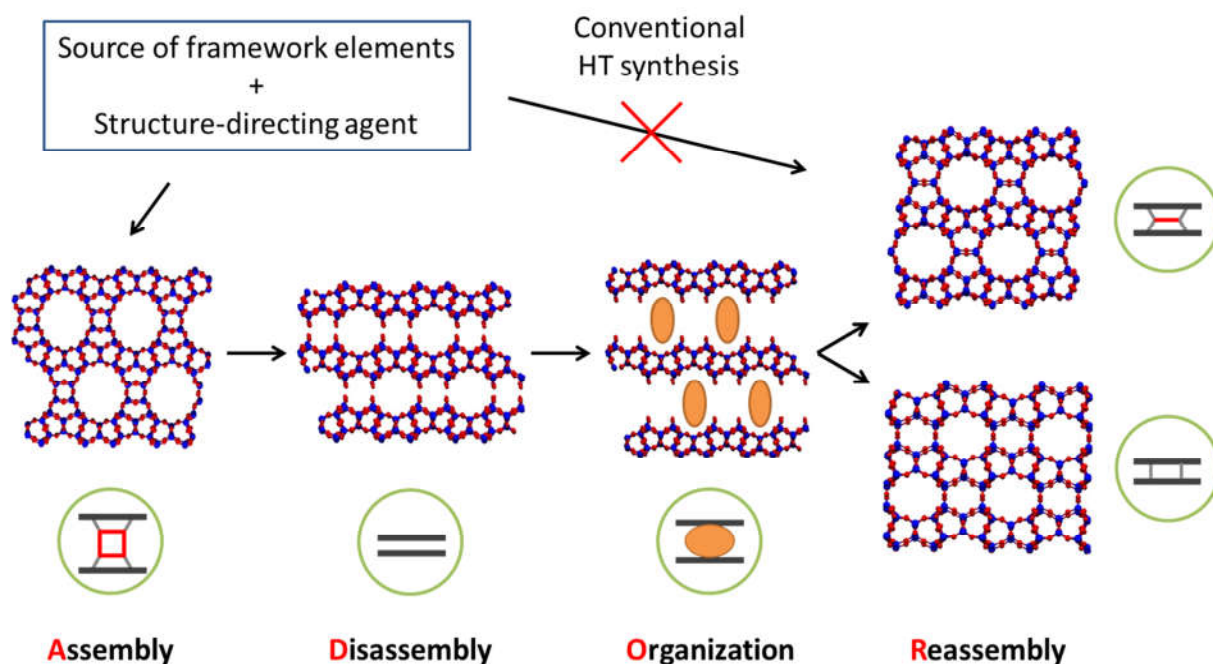


Fig. 2. Schematic representation of the multistep ADOR (assembly-disassembly-organization-reassembly) approach.

Until 2017, the key issue of the ADOR approach was its general applicability, until then not yet demonstrated, because this new synthetic protocol had focused on the application of UTL as the starting zeolite, though other materials had already been disassembled successfully. UTL germanosilicate was an perfect ADOR initial structure thanks to its framework composition and to the stability of the 2D building blocks that are formed upon disassembly. More recently, we reported the preparation of a novel zeolite, designated as IPC-12, via the ADOR treatment of UOV as the starting germanosilicate zeolite (*Angew. Chem. Int. Ed.* 2017). UOV has been previously predicted as a good target (*Trachta et al. ChemPhysChem* 2014, 15, 2972). However, due to its in three-dimensional pores, in contrast to two-dimensional pores appeared in UTL, the porous layers presented in UOV could be less stable if compared to that of UTL. In planning this protocol, the following factors, which control the ADOR process, must be considered: appropriate nature (composition) and type (topology) of the initial zeolite framework and optimized parameters for post-synthesis disassembly and reassembly of layered precursors, among others. The structure of the novel IPC-12 zeolite was confirmed by XRD and STEM-HAADF microscopy with near-atomic resolution (Fig. 3).

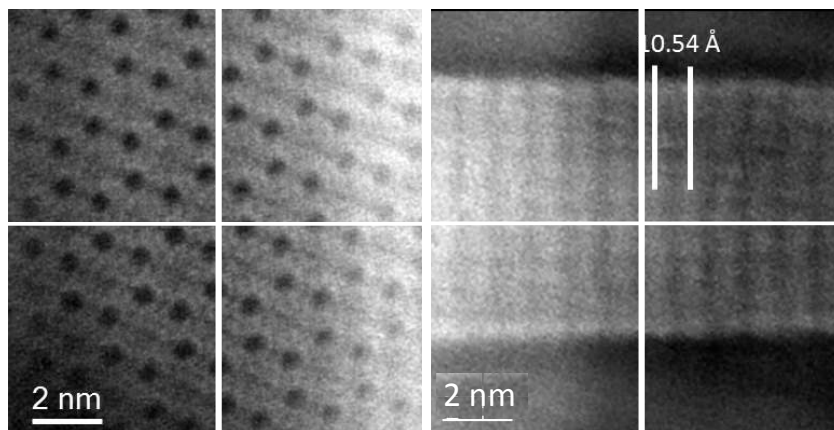
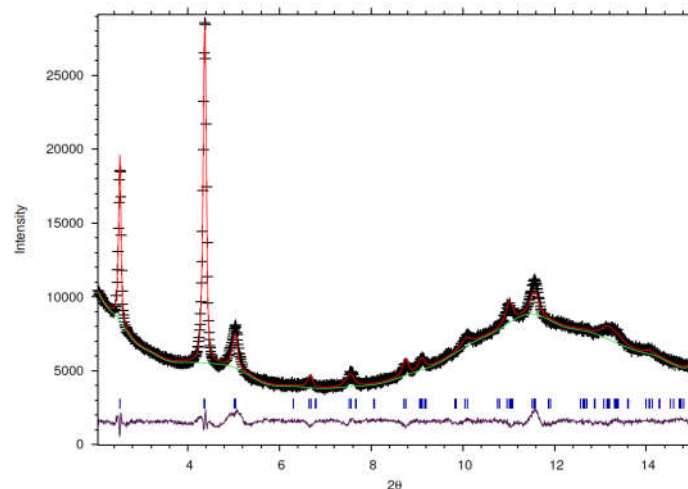


Fig. 3. (from *Angew. Chem. Int. Ed.* 2017) top – experimental XRD (obtained using synchrotron source) for IPC-12 (crosses), respective calculated diffractogram (red line) from the final Rietveld refinement, and differential pattern between the experimental and predicted data (purple line); bottom – spherical aberration corrected STEM-HAADF images of IPC-12 in the projection *ab* demonstrating the presence of 12-ring channels (left) in the projection *ac* displaying the organization of lamellae in the product of ADOR transformation, with corresponding interlayer distance of ~ 10.5 Å (right).

In the following study, we showed how conventional synthesis under hydrothermal conditions and the ADOR procedure can be combined (*Chem. Mater.* 2017) by producing a parent zeolite (SAZ-1) via hydrothermal synthesis specifically targeting a novel zeolite appropriate for further transformation by ADOR (Fig. 4), thereby amplifying the number of new zeolites that can be derived from a single hydrothermal preparation: instead of providing only one new zeolite for each successful synthesis, we showed how the single assembly process (synthesis under hydrothermal conditions) could provide three novel zeolites, an initial and two derivatives (IPC-15 and IPC-16) having different framework

types. Despite derived materials possess channel sizes different to the starting SAZ-1, the structures of their layers are very similar because the produced structures are propagated from the initial zeolite. Thus, this family of materials forms an isorecticular series of zeolites with the closely related framework topologies.

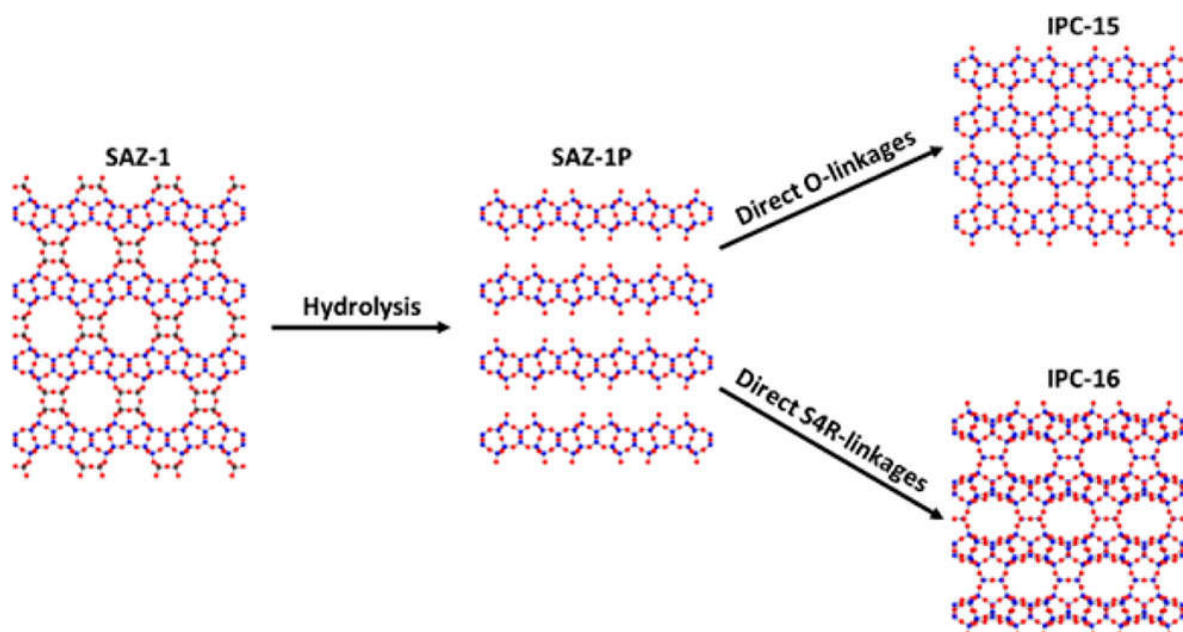


Fig. 4. (from *Chem. Mater.* 2017) ADOR scheme for SAZ-1 zeolite showing the formation of layered intermediate and the products of its condensation either by direct oxygen interlayer linkages (formation of IPC-15) or by additional S4R building units (IPC-16 zeolite). All structures are viewed along the c-axis.

Thus, firstly used for zeolites with UTL topology, ADOR has recently been extended to other germanosilicates, such as UOV and SAZ-1. Due to the predetermined mechanism of layer formation and to the possibility of preparing new structural types of 2D zeolites, the top-down (ADOR) approach can be considered a good alternative to direct hydrothermal methods.

Adjusting the properties of zeolites using post-synthesis top-down approaches

(Representative publications on this topic: *Catal. Sci. Technol.* 5 (2015) 2973–2984; *Chem. Eur. J.* 22 (2016) 17377–17386; *ACS Catal.* (2019) DOI: 10.1021/acscatal.9b00950)

Direct hydrothermal synthesis is the most frequently used method for the modification of the chemical composition and hence nature and concentration of active sites in zeolite catalysts, thus controlling their behavior in a specific catalytic process. Notwithstanding its widespread use, hydrothermal synthesis often limits the maximum concentration of

isomorphously substituted elements in some zeolites, by either restricting the amount of cations that fit into zeolite voids and compensate framework charge or accelerating the formation of undesired phases from reaction mixtures with non-optimal chemical composition.

In turn, post-synthesis isomorphous substitution is not only an alternative to direct hydrothermal crystallization but also a facile approach in broadening the limits of heteroelement incorporation. Traditionally, heteroelements can be incorporated after treating the preliminary prepared zeolite by means of i) gas-phase isomorphous substitution using a volatile heteroelement source at elevated temperature or ii) hydrothermal isomorphous substitution using solutions of a heteroelement source with different pH at a moderate temperature. Furthermore, solid-state reactions can be used to tailor the chemical composition of zeolites. Removing some framework atoms (demetallation, especially degermanation) leads to the “silanol nests” formation that usually takes place before the incorporation of heteroelements.

Ge acts as an inorganic structure-directing agent selective to frameworks containing D3R and D4R units with small rings. This finding catalyzed the discovery of numerous germanosilicate zeolites, including extra-large pore zeolites (*Chem. Soc. Rev.* 2019). Such zeolites have high potential for the catalytic conversion of bulky molecules. However, their synthesis requires developing alternative approaches for isomorphous substitution in order to decrease the cost of germanosilicate zeolites and to enhance their hydrolytic stability, thereby enabling the practical use of their attractive features. In the last decade, considerable research efforts have been made to meet these requirements for post-synthesis isomorphous substitution in germanosilicate zeolites (Fig. 5).

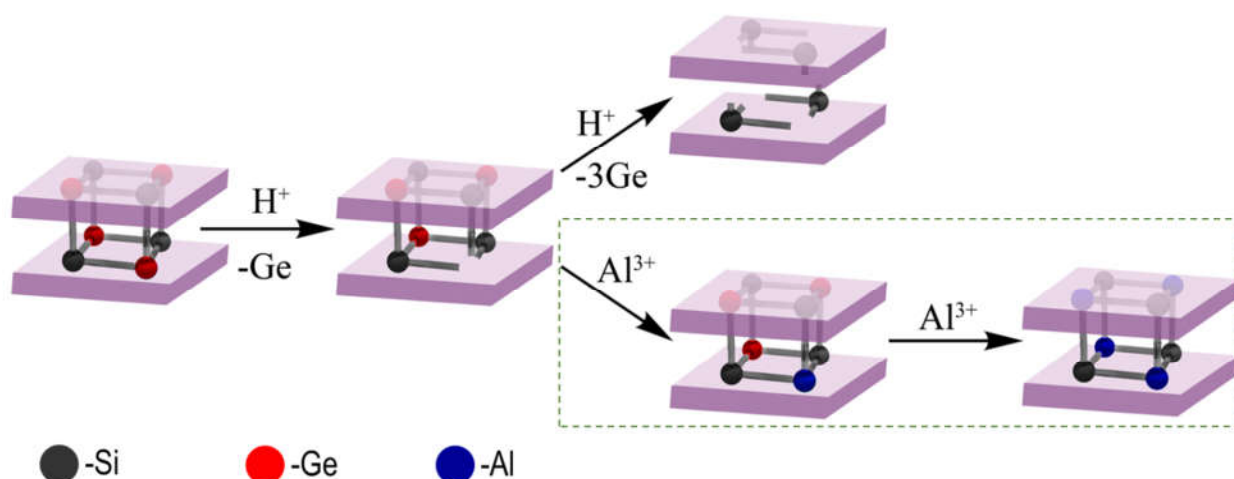


Fig. 5. Degermanation (top reaction route) or degermanation-metalation (in particular, aluminations, bottom route) process resulting in the isomorphous substitution of Ge with other elements.

Our recent studies on this topic have primarily aimed to improve the hydrolytic stability and to tailor the acidity of germanosilicates having anisotropic distribution of Ge-rich D4Rs, i.e., zeolites ITH and UOV with medium-size pores (*Chem. Mater.* 2014; *Catal. Sci. Technol.* 2015; *J. Energy Chem.* 2016, *Dalton Trans.* 2018), as well as extra-large pore UTL (*Chem. Eur. J.* 2016). The frameworks of all these zeolites can be regarded as silica lamellas linked by D4R units. The Si/Ge ratio in the parent germanosilicate zeolites determines the number of labile Ge–OT bonds, strongly affecting their hydrolytic stability. One of the most interesting features of Ge-rich zeolites (Si/Ge < 6 for ITH, UOV and Si/Ge < 8.5 for UTL) is the disassembly of their frameworks with the formation of crystalline nanolayered materials, enabling various treatments for modifying layer orientation and spacing (see the discussion in previous section devoted to ADOR transformation). When disassembling under heteroelement-free acidic conditions, Ge-poor ITH and UOV zeolites maintain their structural ordering if treated with Al-containing acidic solutions, thus highlighting the stabilizing effect of Al by rapidly healing silanol defects resulting from the hydrolysis of Ge–OSi bonds. ²⁷Al MAS NMR revealed the preferential introduction of Al atoms into framework positions (80 – 90 % of Al atoms were tetrahedrally coordinated) of germanosilicate zeolites upon the treatment with Al(NO₃)₃. However, the concentration of Al depends on both treatment conditions and chemical composition, crystal size, and topology of the initial germanosilicate. Accordingly, the amount of Al introduced into the framework increases when rising 1) Al(NO₃)₃ concentration (0.1 – 1 M), 2) pH (0.5 – 2) or 3) treatment temperature (25 – 175 °C). A marked increase (up to 2.5 times) in the amount of Brønsted acid sites at a slightly decreased concentration of Lewis acid centers was observed when increasing the alumination temperature from 80 to 175 °C, regardless of the topology and chemical composition of the initial germanosilicate. This effect was associated with the enhanced relative rate of the condensation (formation of Si–O–Al bonds) over the hydrolysis of Ge–O linkages at higher temperatures.

As the concentration of Al in aluminated zeolites increases, the Ge content decreases. This decrease in Ge concentration in Ge-poor zeolites (Si/Ge > 6) is approximately proportional to the amount of Al introduced into the framework but markedly exceeds the concentration of Al incorporated into Ge-rich samples (Si/Ge < 6). Such non-equivalent exchange of Ge for Al makes it possible to modify the textural characteristics of Ge-rich zeolites in parallel with post-synthesis isomorphous substitution. In particular, mesopores have been developed by alumination of Ge-rich ITH and UOV zeolites, yielding hydrolytically stable hierarchical micro-mesoporous aluminosilicates. Thus, post-synthesis substitution of Ge for Al in the medium-pore Ge-rich ITH zeolite not only resulted in the formation of strong Brønsted acid sites but also enhanced their accessibility in comparison with heteroelement-substituted ITH zeolites prepared using direct template-assisted crystallization. In turn, the textural characteristics of Ge-poor zeolites lacking extractable Ge atoms were not significantly changed during the alumination.

In contrast to other germanosilicates with unidirectional location of Ge-rich D4R units, introducing Al into the framework did stabilize the extra-large pore UTL zeolite under acidic conditions. This particular behavior of UTL can be explained by fast hydrolysis of interlayer bonds combined with restrictions for Al incorporation into neighboring positions of the zeolite framework. Nevertheless, consecutive Ge-to-Si substitution, followed by alumination makes it possible to not only enhance the hydrolytic stability of UTL zeolite but also generate a high amount of strong Brønsted and Lewis acid sites, significantly exceeding the values ever found for Al-containing UTL synthesized directly. As for other Ge-rich zeolites, UTL subjected to post-synthesis alumination shows an increased fraction of mesopores. Ge substitution for Al in Ge-rich UTL zeolite enhances their hydrolytic stability, in line with the lower reactivity of Si–O–Al vs. Si–O–Ge bonds.

Improving the acidity and mesoporosity of aluminated germanosilicate zeolites naturally enhanced their catalytic performance. In a model reaction of propanol tetrahydropyranlation, the increase in the amount of strong acid centers markedly increased the activity of aluminated ITH (yield reached 40 %), IWW and UTL (up to 80 % product yield for both) contrary to the virtually non-active starting germanosilicate zeolites. Formation of mesopores upon the post-synthetic Al-treatment of the Ge-rich ITH zeolite increased the activity of the corresponding material with micro-/mesoporosity in alcohols tetrahydropyranlation compared to the purely microporous Al-ITH material with comparable chemical composition and synthesized directly (40 vs. 20 % yield, *Catal. Today* 2016).

Hence, isomorphous substitution in germanosilicates by post-synthesis is a straightforward and efficient method for modifying their acid properties while enabling the design of hydrolytically stable catalytic materials. Consequent recycling of germanium can accordingly improve the potential of the large-scale use of Ge-containing zeolites substituted with heteroelements of different nature. By using Ge-rich zeolites as starting materials, the textural characteristics of zeolites can also be modified, thus producing hierarchical micro-mesoporous catalysts, whereas acidic hydrolysis of Ge-rich zeolites results in new layered crystalline materials, which can be further condensed into 3D frameworks or transformed into expanded structures by different post-synthesis modifications.

Recently, the combination of ADOR method with post-synthetic degermanation-aluminum incorporation for the synthesis of Al-IPC isorecticular zeolites was reported for the first time (*ACS Catal* 2019), thereby synthesizing a set of Al-IPC-n aluminosilicates (Fig. 6) with the same crystal shape and size, content of aluminum and amount of acid centers (0.385 ± 0.015 mmol/g) but having non-equal location of acid centers and different size of the pores.

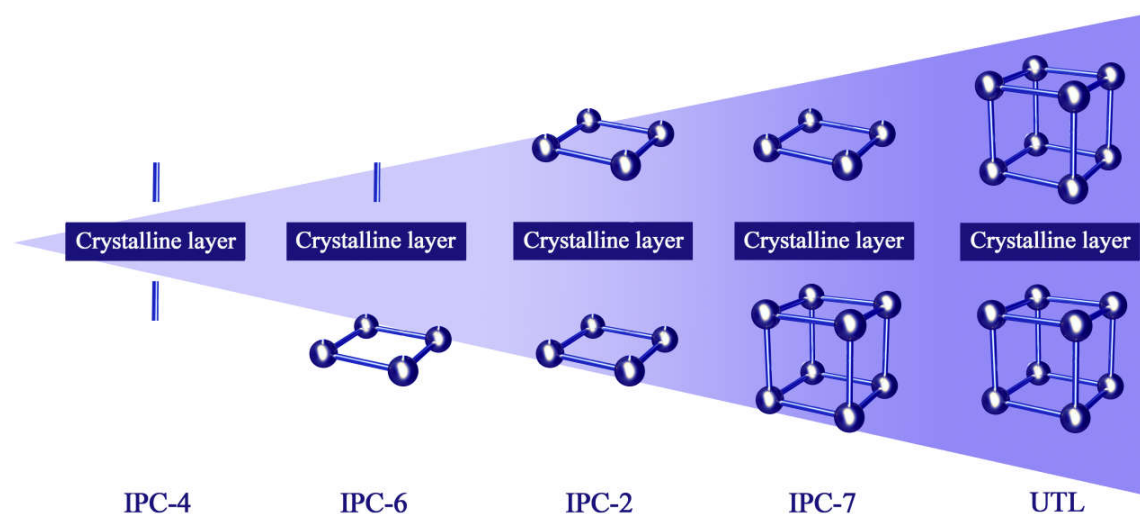


Fig. 6. (from *ACS Catal.* 2019) Schematic representation of the difference in the structure of units linking the lamellas having the same topology in the family isorecticular IPC-n zeolites (spheres represent T atoms (Si, Al, Ge), whereas lines represent oxygen bridges).

IR spectroscopic study after adsorption of probes of different size (d3-acetonitrile, quinoline) has demonstrated that the amount of acid centers on the outer surface and located in 14-ring channels (“external” acid sites) decreases as IPC-7 (35 %) > IPC-2 (29 %) > IPC-6 (25%) > IPC-4 (21 %). An kinetic study on ethanol-to-diethyl ether transformation revealed the limited confinement of dimeric alcohol adduct in IPC-6 and IPC-4 ($k_{\text{first}} = 0.4 - 0.9 \text{ mol}_{\text{DEE}}/(\text{mol}_{\text{H}^+} \text{ bar s})$) in comparison with IPC-2 ($k_{\text{first}} = 3.8$) and especially in IPC-7 ($k_{\text{first}} = 6.3$) zeolites. The increased content of Al atoms in 10-ring pores of IPC-7 may explain why the transition state stabilization is higher in comparison with hydrogen-bonded and a gaseous ethanol molecules in IPC-7 vs. IPC-2 zeolite. Furthermore, despite showing comparable activity in ethanol tetrahydropyranlation, the performance of IPC-n materials in the reaction of large-size 1-decanol was significantly different, improving with the fraction of “external” acid centers as IPC-4 < IPC-6 < IPC-2 < IPC-7; that is, with the increase in pore size in the aforementioned zeolites.

The comparison of the activity of the IPC-6 material and IPC-2/IPC-4 zeolites mixture (two catalysts having the same adsorption characteristics and overall amount of acid centers but differing in the location of active sites as discussed above) allows to relate the number of “external” acid centers to the catalytic behaviour in the tetrahydropyranlation of large-size 1-decanol. IPC-6 possesses lower concentration of mentioned sites, and therefore exhibited poorer catalytic performance compared to IPC-2/IPC-4 mixture, despite having the same sorption and bulk acidic properties. These observations not only evidence the direct relation between zeolites activity in liquid phase reactions and the acid centers localization together with the type of micropore system, but provide excellent model materials (Al-IPC-n) to study the key confinement effects in zeolite-catalyzed processes.

Development of hybrid organic-inorganic solids with tunable textural properties

(Representative publications on this topic: *J. Am. Chem. Soc.* 136 (2014) 2511 – 2519; *ChemPlusChem* 80 (2015) 599–605; *Chem. Sci.* 7(2016) 3589–3601)

Porous hybrids and nanostructured composite materials comprise the benefits of individual constituents and additional characteristics unique for practical use. In the past decade, several types of organic-inorganic hybrids have been extensively studied, in particular, metal-organic frameworks and organic-silicate materials (either microporous or hierarchical). In addition to anchoring by post-synthesis, an approach used to prepare multifunctional hybrids, most methods for design of nanostructured organic-inorganic frameworks reported thus far are grounded on the direct synthesis. The latter method suggests the self-organization of building units (usually SDA-assisted process) to produce materials having specified properties and precludes a fine tuning of the structure and porous characteristics of desired hybrids.

Utilization of the IPC-1P, lamellar precursor produced using UTL germanosilicate, allows us to produce organic-inorganic hybrid materials with adjustable adsorption properties (*JACS* 2014). The rationale of these manipulations with lamellas and linkages between the layers is summarized in Fig. 7. The process starts with the assembly of the germanosilicate (Fig. 7, 1st step) possessing chemically labile and selectively located structural units. Following disassembly of germanosilicate with suitable chemical composition offers layered building-blocks (2nd step on Fig. 7) similarly to ADOR process. Obtained fragments can be swollen (3th step on Fig. 7) to efficiently separate the 2D units, thereby providing the voids for introduction of the organic/inorganic precursors into the interlayer space (step 4 on Fig. 7). The precursor have to be hydrolyzed (5th step on Fig. 7), while surfactant used for the swelling need to be extracted on the last step (6th on Fig. 7).

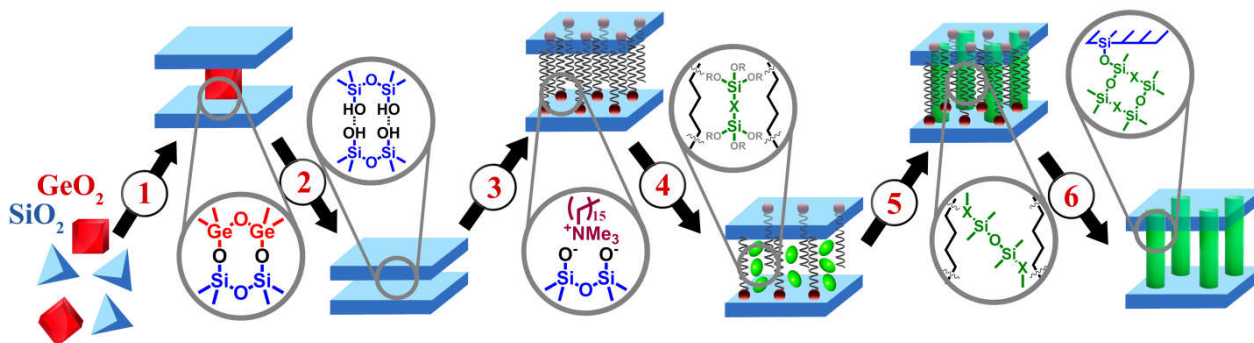


Fig. 7. (from *Chem. Sci.* 2016) Sequence of the steps (1 – zeolite assembly, 2 – controllable deconstruction, 3 – interlayer expansion, 4 – incorporation of pillars' precursor, 5 – subsequent hydrolysis, 6 – surfactant extraction), from low-molecular precursors to organic-inorganic hybrids.

Hybrids possessing particular functionality have been prepared by this method and utilized as catalysts in liquid-phase reactions (*ChemPlusChem* 2015). One of the advantages of resulting hybrid solids designed using this strategy is the ability to adjust their porous characteristics (i.e., BET area and micropore/mesopore volumes) by variation of synthesis parameters. To understand the effect of the nature of organic linker on the physico-chemical properties of the resulting materials, different silsesquioxanes and polyhedral oligomeric siloxanes have been used to construct the interlayer pillars (*Chem. Sci.* 2016). They can be grouped based on i) type of the organic linker (having either exclusively carbon in the molecule backbone or also sulfur/nitrogen); ii) size of the Alk- or Ar-bis(trialkoxysilyl) linkers; iii) maximum number of covalent bonds (denticity) that particular silane can form (2 – 6); iv) rigidity of the chain (different e.g. for systems containing only sp^3 or both sp^3 and sp^2 /aromatic carbon atoms); and v) nature and bulkiness of the alkoxy-group in initial silane. The effect of tetraethylortosilicate addition (used as binding agent) on the ordering and porosity of resulting hybrid materials was also studied. In summary, the effects of the type of linkers (e.g., composition, chain length, denticity and flexibility, among others) on the structure and textural characteristics of obtained hybrids has been studied in depth to develop hybrid materials with functional groups, as further detailed below.

The lengthening of aliphatic hydrocarbon chain leads to reduction of interlayer distance, BET area, and volume of pores in resulting hybrids. These changes can be explained by the decrease in the rigidity of large-size linkers, which provides twisting and shrinking of pillaring units. The latter results in the detected difference in d-spacing and textural (S_{BET} , V_{total}) characteristics. Contrary to Alk-containing silanes, no drastic changes in the properties of hybrid materials were found when changing the size of Ar-containing linkers. These aryl-containing linkers behave differently from their alkyl analogs due to their much higher rigidity.

The denticity of linkers defines the limit in the number of covalent bonds that respective unit can form with other molecules or pillars or atoms of the zeolite constituent. When using short-chain linkers containing unsaturated bonds, no significant disordering is observed in the layer arrangement after decreasing the denticity, but d-spacing and porous characteristics decrease sharply. The significant amounts of micropores instead of mesopores, together with the mismatch between adsorption and desorption branches of adsorption isotherms, indicate the low rigidity of interlayer props consisted of a building-blocks with low denticity. This phenomenon is stronger when using bulkier Ar-linkers – the utilization of a bidentate aromatic silanes results in the obtaining of low-porous hybrids. Decreasing the denticity of the linker may generate additional micropores if utilizing relatively small linker molecules (preserving structure using limited number of connections) as organic precursors. However, preparing interlayer props while retaining interlamellar distance typically needs precursors with maximal denticity, especially when large-size silanes are applied.

To assess the direct effect of linker flexibility on the textural characteristics of designed hybrids, short- (C_2) and long-chain (C_8) precursors have been used to compare saturated alkyl-containing precursors with their vinyl C_2 analogs and a flexible linker with an aromatic C_8 . Hybrid materials obtained using silanes containing C_2 -chains exhibited comparable structural (according to the XRD data) and textural properties (type of adsorption isotherms and S_{BET}/V_{total} characteristics) but differ in the fraction meso- and macropores of a large size, which increases when using more rigid vinylene linkers. Conversely, a material with a more flexible C_8 -chain shows significant decreases in d-spacing and pore volume combined with a discrepancy between ad/desorption branches of isotherm similar to that described for the linkers of different denticity. Nevertheless, both materials display isotherm with similar shapes and a high relative content of micropores.

A combination of functional silane and “binder” (e.g. TEOS) can be used to improve the stability of interlamellar pillars after processing of the layered precursor because without this additive linkers possessing long-chain backbone or low denticity provide limited structural order causing poor textural characteristics. If binder is added, the structure ordering is maintaining (if TEOS-free synthesis leads to the formation of stable organic pillars) or improving (if TEOS-free hybrid was highly disordered). The positions of interlayer peaks in XRD patterns of latter materials shift towards the $2\theta = 2.5 - 2.6^\circ$ typical for swollen materials applied for the incorporation of the linker, thus highlighting the higher rigidity of props formed by both functionalized silane and TEOS against the structural rearrangement after SDA extraction.

These hybrid organic-inorganic materials differ in porosity (channel size and volume of pores) and type of functional groups in organic constituent, which is defined by the structure of initial silane; accordingly, hybrids can be applied for different sorption- and catalysis-related applications. To demonstrate the enhanced catalytic potential of such hybrids, selected materials were compared in Knoevenagel reaction with the purely inorganic material IPC-1PI containing silica pillars (obtained by the same approach as organic props but utilizing TEOS instead of silanes). Materials under investigation had similar void volume ($0.4 - 0.5 \text{ cm}^3/\text{g}$) and surface area ($400 - 700 \text{ m}^2/\text{g}$) but different chemical linkages connecting zeolitic lamellas: organic (purely carbon or nitrogen-doped) linkers in hybrids and silica props in IPC-1PI. The alteration in the pillars nature became decisive for catalytic behaviour: the materials without functional groups showed negligible benzaldehyde conversion ($< 5\%$ after 2 h), whereas the N-containing hybrids provided $>99\%$ yield of targeted condensation product at the same reaction time and temperature. Such result exemplifies the ability to adjust the chemical and porous characteristics of hierarchical organic-inorganic hybrid solids, which can be utilized for various applications.

Application of metal-organic frameworks as catalysts in liquid phase reactions

(Representative publications on this topic: *Adv. Synth. Catal.* 355 (2013) 247–268; *ChemSusChem* 6 (2013) 865–871; *Catal. Tod.* 243 (2015) 2–9)

Transition metal salts have long been applied as active catalysts for various reactions, including those used in industrial processes. However, homogeneous catalysts are difficult to recover or reuse. This drawback can be solved by use of MOFs – microporous organic-inorganic materials composed of metal ions or clusters, which are connected in the framework by polydentate linkers of various functionality. MOFs as heterogeneous catalysts offer substantial benefits in comparison with their homogeneous counterparts. In addition to possibility of easy recovery and reuse, their use lead to minimization of waste, as shown in studies on the MOFs characterization and application in catalysis (*Metal-Organic Frameworks: Applications in Separations and Catalysis*, 2018). The well-defined node-linker arrangement in these materials accounts for the development of an ordered framework and for the existence of channel systems of different geometry in MOFs. Simultaneously, coordination bonds with medium energy values, weaker than covalent bonds but stronger than Van der Waals interactions, are chemically labile upon treatment with aggressive substances (e.g., used in catalytic cycle) or thermally unstable under the conditions used for catalysis (*ChemCatChem* 2013). However, MOFs containing channels with aperture larger than 1 nm have well-developed surface area and large void volume that is crucial for overcoming diffusional limitations typically found in conventional small-pore solid catalysts such as zeolites.

Based on the above, MOFs are potentially better heterogeneous catalysts than traditional zeolites or other microporous materials used as the catalysts for the processes carried out at low temperature in liquid phase thanks to the relatively simple design of MOFs containing preferred types of metal and linker, to their large amount of acid or base centers and to their porous characteristics, as shown in several studies comparing the catalytic behaviour of MOFs with that of microporous and even hierarchical zeolites (*ChemCatChem* 2013, *Catal. Today* 2013, *Catal. Sci. Technol.* 2013, *ChemSusChem* 2013, *Adv. Synth. Catal.* 2013, *ChemCatChem* 2013, *Catal. Sci. Technol.* 2013, *Front. Chem.* 2013, *Dalton Trans.* 2014, *Catal. Tod.* 2015, *Catal. Tod.* 2015, *Micropor. Mesopor. Mater.* 2015, *ChemPlusChem* 2016, *ChemPlusChem* 2017, *Inorg. Chem.* 2018, *Catal. Lett.* 2018). For a simpler and more direct comparison, only outcomes associated with iron-containing MIL-100 and HKUST-1 ($\text{Cu}_3(\text{BTC})_2$) as representative MOFs and Beta and USY as conventional zeolite materials are discussed here. The respective reactions (Pechmann condensation, Beckmann rearrangement, Knoevenagel condensation, Prins addition and annulation reaction of phenols with methylbutenol, Fig. 8) result in formation of commercially valuable substances or those used as intermediates for production of biologically active compounds.

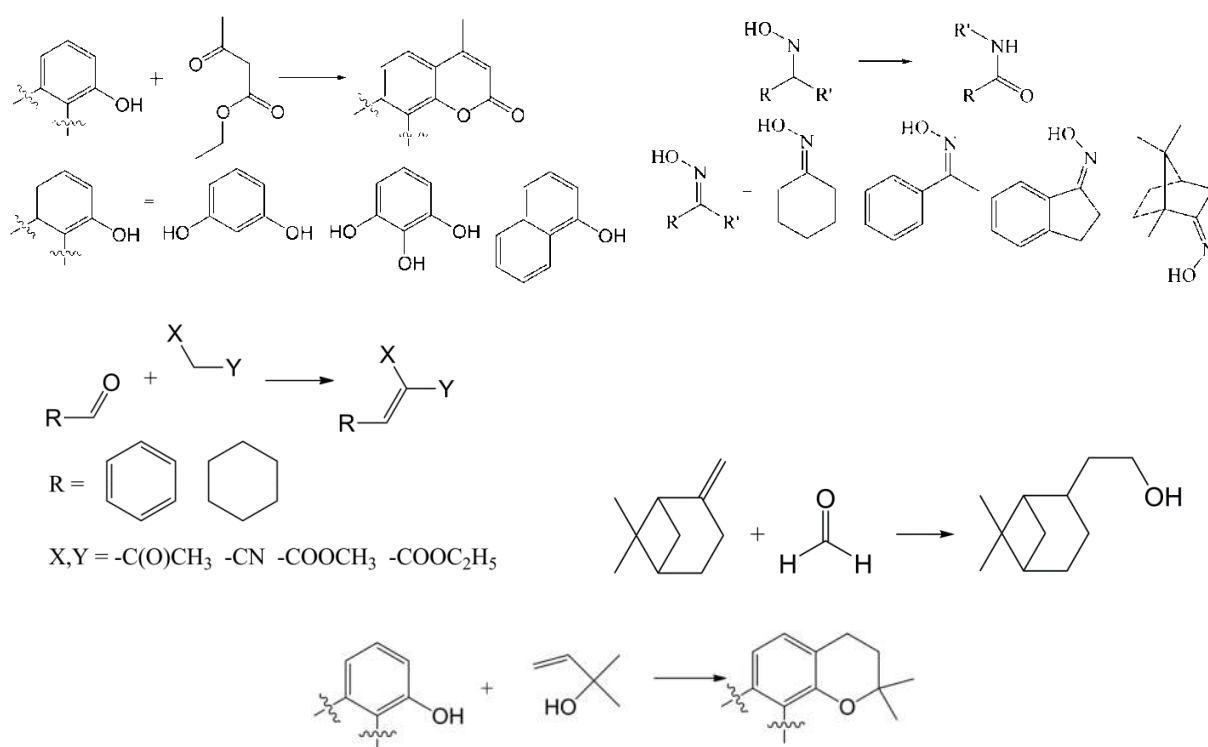


Fig. 8. Reactions used to compare the catalytic activity of MOFs and conventional zeolite materials (top: Pechmann condensation (left), Beckmann rearrangement (right), middle: Knoevenagel condensation (left), Prins reaction (right), bottom: annulation reaction of phenols with methylbutenol).

Opposing to zeolites, MOFs enable only very low conversion of phenols containing two or three hydroxyl groups to the targeted products (selectivity did not exceed 1 %) in Pechmann condensation, whereas 1-naphthol conversion over Cu- and Fe-MOF were up to 90 % (selectivity to the targeted coumarin reached 95 %) after 24 h. Preservation of MOF framework during catalysis was shown by XRD. Conversely, the framework of Cu-MOF was decomposed when interacting with pyrogallol at these reaction conditions. Based on the detection of MOF lattice debris (trimesic acid) in solution after catalysis, a substitution of trimesate linkers due to the simultaneous interaction of metal clusters in MOF with two hydroxyl groups of pyrogallol with further replacement of linker by remaining hydroxyl group of phenol was proposed. Similarly, the decreased activity of Cu- and Fe-MOFs in the condensation of resorcinol is caused by the strong substrate adsorption on the coordinatively unsaturated sites, thereby blocking them. In 1-naphthol, these interactions were not expected because the substrate molecule had just one hydroxyl group. Thus, the concerted effect of the adjacent active centers was hypothesized to explain why 1-naphthol transformation over MOFs is considerably faster than over zeolites. Pechmann reaction is bimolecular process, and reactants can interact with the active centers situated in the one

cavity of MOF, resulting in formation of closely located adsorption complexes facilitating further reaction. Such an interaction of a reactants can occur because the active sites in MOF are in close proximity (the distance between metal centers is approximately 8 Å). In addition, their high regularity and concentration and the large size of the pores and cavities also contribute to this direct interaction.

Four substrates with different sizes and reactivities (cyclohexanone oxime, acetophenone oxime, 1-indanone oxime and camphor oxime) have been used to compare the catalytic behaviour of traditional zeolites Beta and USY with those of $\text{Cu}_3(\text{BTC})_2$ in the Beckmann rearrangement. Except for the bulkiest camphor oxime (with the size of the molecule 7.5 x 6.7 x 6.5 Å), the rearrangement of smaller molecules (with kinetic diameters of 7.8 x 5.3, 9.0 x 5.4 and 9.2 x 5.4 Å, for cyclohexanone, acetophenone and 1-indanone oximes respectively), over zeolites Beta and USY proceeded with higher targeted substances yields than on Cu-MOF. Regardless of the large amount and high accessibility of coordinatively unsaturated sites in MOF, transformation of smallest oxime on $\text{Cu}_3(\text{BTC})_2$ was less efficient in comparison with Beta and USY. In contrast to cyclohexanone oxime, reactant conversions were significantly higher, with 100% selectivity, for acetophenone and 1-indanone oximes. Accordingly, electron-rich Ar group migrates more easily than the Alk one towards the oximino N-atom. Reaction intermediate stabilization by the Ar group accelerated the transformation of acetophenone and 1-indanone oximes, which was much faster than in the reaction with the aliphatic cyclohexanone oxime. Acetophenone oxime conversion rates have the same trend as those for cyclohexanone oxime: $\text{Cu}_3(\text{BTC})_2 \leq \text{Beta} < \text{USY}$. The conversions of the bulkier 1-indanone oxime were lower than that of acetophenone oxime (54 – 60 % vs. 81 – 94 %) using USY and Cu-MOF. In contrast, the conversion rates of the transformation of both acetophenone and 1-indanone oxime over zeolite Beta under the same conditions were virtually identical (64 vs. 65 %), hence clearly demonstrating the participation of acid centers on the outer surface/mesopores in this catalytic process.

The size effect was even stronger when using the camphor oxime, which had the largest kinetic diameter of all substrates used in this study. Zeolite Beta was practically inactive in the rearrangement of camphor oxime, whereas USY and Cu-MOF showed acceptable conversions (up to 35 %). Camphor oxime fragmentation to nitriles and side processes involving targeted δ -lactam considerably influence the overall reaction output at such conditions. As a result, the resulting complex mixture was analyzed only in terms of conversion. Camphor oxime transformation most likely occurs on the external surface/in the channel entrances for all materials used as the kinetic diameter of the reactant exceeds the pore size of the catalysts. Consequently, camphor oxime is not able to enter the channels and get to the acid centers of catalysts such as zeolite Beta. Both Cu-MOF and USY had been active in the camphor oxime rearrangement thanks to the suitable diameter/curvature of their pore windows, which allowed the interaction between the reactant and the acid center. However, the concentration of active centers in the mesopore

entrances, which result from dealumination and steaming, were lower in the USY than in $\text{Cu}_3(\text{BTC})_2$, which may explain more efficient transformation of camphor oxime on the Cu-MOF (34 vs. 23 % for MOF vs. zeolite). Thus, as detailed above, the catalytic behaviour of both zeolites and MOF in oximes rearrangements depends on the sizes of pores and substrates due to the gradual increase in the involvement of outer active centers, ranging from a minor effect on cyclohexanone oxime to a dominant effect on camphor oxime.

In the Knoevenagel reaction between aliphatic or aromatic aldehyde with ethyl acetoacetate, Beta zeolite exhibited moderate yields of targeted substances (up to 40 %) while Fe-containing MIL-100 demonstrated lower yields (< 15 %) at high conversion (> 99 % after 1 d, 130 °C). This low selectivity observed for Fe-MOF results from a side reaction (secondary condensation of the reaction product with ethyl acetoacetate). In aldehyde condensation, substrate conversion was higher with methyl cyanoacetate than with ethyl acetoacetate, regardless of the catalyst used, but especially over MIL-100(Fe), which enabled > 99 % yields of targeted product. Conversely, Beta and $\text{Cu}_3(\text{BTC})_2$ led to yields in the range 30 – 70 %. These differences were explained by the increased reactivity of the methyl cyanoacetate in studied reaction and by the increased stability of the targeted compound, which was more resistant to further transformations. Although benzaldehyde condensation with malononitrile on Fe- and Cu-MOFs at moderate temperature (80 °C) had been finished after 1 h (> 99 % targeted substance yields), only 60 % yield was observed on Beta zeolite, even at prolonged reaction time (5 h) at the same temperature. The order of relative catalytic activity changed because more weak active centers (in MOFs) suffice to catalyze the reaction with a more reactive substrate (malononitrile). Once strong acid sites are not required, the catalytic behaviour is defined by accessibility of those centers and their amount. Superiority of MOFs compared to zeolites in void volume and concentration of accessible acid centers fail to account for differences in the MOF/zeolite catalytic activity at a low-temperature range (< 80 °C). At mentioned conditions, $\text{Cu}_3(\text{BTC})_2$ and MIL-100(Fe) show much higher initial reaction rates of Knoevenagel reaction than zeolite. Product yield reached 100 % over Cu- and Fe-MOF, but the condensation did not occurred on zeolites (conversion < 1 %). The preservation of MOF lattice and the possibility to regenerate the catalyst were confirmed when comparing diffractograms before/after catalytic runs and when performing leaching and reusability tests. Cyano-groups presented in malononitrile molecule may simultaneously interact with adjacent Cu or Fe ions in the MOF lattice, thus explaining the particularly high conversion rates over Cu- and Fe-MOF assessed in reactions of Alk- and Ar-aldehyde with malononitrile. The interaction energy of such an adsorption complex is presumably higher in comparison with the complex obtained on a single metal center, hence decreasing the activation energy for Knoevenagel reaction on MOFs studied.

The activities of Cu and Fe-MOFs as well as Beta and USY zeolites were compared in the Prins reaction between β -pinene and formaldehyde in which nopol is the target product of the reaction. In contrast to Fe-MOF, which has mild acid sites, undesired products

(predominantly, β -pinene isomers, camphene and limonene, with 10 – 40 % selectivity) formed when zeolites Beta or USY are applied due to the relatively strong Brønsted acid sites of zeolites, thus spoiling their catalytic behaviour in this condensation reaction. Over MIL-100(Fe), the yield of nopol (51 < 64 < 68 < 82 %) directly increased with the increase in relative solvent (dodecane, p-xylene, cyclohexanone, acetonitrile) polarity (0 < 0.074 < 0.281 < 0.46). Over $\text{Cu}_3(\text{BTC})_2$, β -pinene conversion was 40 %, albeit with low selectivity (7 %) to nopol. Unexpectedly, the dominant product of Prins reaction on Cu-MOF was camphene, while this product was not detected in reaction mixtures after catalytic runs using other MOFs. The full picture for the formation of such side product is not completely clear because at the same conditions Fe-MOF provides selective transformation of β -pinene to nopol. Thus, the latter catalyst exhibited the highest activity in Prins reaction of all catalysts tested in this study, most likely because of the possessing of large-size mesoporous voids, which provide an appropriate reaction space for nopol formation. The catalyst can be used in 3 catalytic runs without losing activity, while preserving the structure order and characteristics of acid centers.

Annulation encompasses a wide range of reactions. For example, phenol C-isoprenylation with 2-methyl-3-buten-2-ol catalyzed by acids proceeds via the 2- and 4-isoprenylphenols formation, followed by cyclization of the intermediate compounds through the intramolecular mechanism. In general, phenol annulation passes via two elementary steps: alkylation in oxygen position and consequent cyclization by the conventional Friedel–Crafts reaction (intramolecular). In turn, carbon-alkylated or oligomerized products are typically formed in side reactions. In this context, phenol and 2-naphthol have been utilized as reactants to assess the effect of the porous characteristics of MOFs/zeolites on their catalytic behaviour in the annulation of phenols with different sizes. MIL-100(Fe) possessing largest void volume and outer surface showed the highest performance (40 – 70 % phenols conversions). In parallel, zeolites have stronger acid centers than MIL-100(Fe). As a result, its catalytic activity is significantly lower due to the interaction of phenols with such acid sites presented in Beta and USY. Conversely, Fe-MOF had higher activity than $\text{Cu}_3(\text{BTC})_2$ thanks to the low acid strength of copper centers. In fact, catalysts containing metal nodes (Lewis sites) with moderate acid strength provided the highest reaction rates because the weaker the metal acid site is, the more unstable the catalyst–reactant complex will be; on the contrary, if the metal node is highly acidic, increased stability of respective adduct is slowing down following transformation. Conversions of 2-naphthol in reaction with methylbutenol on Cu- and Fe-MOF were increased compared to phenol because polymerization partly blocks the pore system of catalysts. 2-naphthol conversion over zeolite Beta was lower than over USY due to slower reactant diffusion in pore systems consisting of relatively narrow channels. Accordingly, the transport pores of USY enabled significantly higher conversion rates of phenols.

Intermediate products (unsaturated ethers, resulting from alkylation/prenylation) and final condensation product – substituted dihydrobenzopyrans (possessing a six-membered

rings) and dihydrobenzofurans (with a five-membered rings) were detected. Dihydrobenzofurans result from the thermal rearrangement of the preliminary formed 6-ring derivatives and are undesired side products. The total selectivity towards pyran/furan products achieved using studied materials were similar, but the regioselectivity varied considerably. The pyranyl-/furan- ratio is much higher in the case of zeolites. For the MOFs, the targeted dihydrobenzopyrans primarily formed on Fe-MOF because the rate of annulation, which produces substituted dihydrobenzopyrans, is lower than the rate of the thermally induced rearrangement in which they are consumed. In addition, MOFs are stable, with no leaching of active sites.

Thus, thanks to the high concentrations of their active sites with well-developed surface, pore volume, mild strength and high uniformity, MOFs are perspective catalytic materials for the processes performed at mild-to-moderate conditions in liquid phase, e.g., Knoevenagel, Pechmann and Prins condensations, Beckmann reaction, and annulation of phenols. These reactions differ in the key characteristic of MOF that provides its catalytic activity.

The first set of reactions, independent of the acid sites strength or type, is nevertheless subtle to the pore diameter in the catalytic material (e.g., rearrangement of oximes and annulation of phenols). Hence, MOFs with better porous characteristics than zeolites showed higher catalytic efficiency in the transformation of large-size reactants. Contrary, zeolite materials exhibited higher activity in processes of small molecules transformation even though their concentrations of acid sites was lower than that of MOFs.

The second set of transformations comprises reactions that predominantly influenced by the nature of the active centers. Low selectivity in reactions involving highly reactive substrates/products (e.g., Prins reaction) is the main drawback of zeolites under such conditions.

The last set of transformations is characterized by the crucial role of interaction of reactants, intermediate substances or final compounds with MOF frameworks and, in particular, acid centers that strongly affect the conversion rates. Similar type of interactions for zeolites was not observed. Therefore, catalytic behaviour of zeolites in such processes is more predictable than that of MOF materials. For the latter, particular substrate-framework interactions may provide either positive (Knoevenagel reaction) or negative (Pechmann condensation) effect on the activity of MOFs as catalysts.
