

Heterogeneous Catalysis in Zeolites, Mesoporous Silica, and Metal–Organic Frameworks

Jie Liang, Zibin Liang, Ruqiang Zou,* and Yanli Zhao*

Crystalline porous materials are important in the development of catalytic systems with high scientific and industrial impact. Zeolites, ordered mesoporous silica, and metal–organic frameworks (MOFs) are three types of porous materials that can be used as heterogeneous catalysts. This review focuses on a comparison of the catalytic activities of zeolites, mesoporous silica, and MOFs. In the first part of the review, the distinctive properties of these porous materials relevant to catalysis are discussed, and the corresponding catalytic reactions are highlighted. In the second part, the catalytic behaviors of zeolites, mesoporous silica, and MOFs in four types of general organic reactions (acid, base, oxidation, and hydrogenation) are compared. The advantages and disadvantages of each porous material for catalytic reactions are summarized. Conclusions and prospects for future development of these porous materials in this field are provided in the last section. This review aims to highlight recent research advancements in zeolites, ordered mesoporous silica, and MOFs for heterogeneous catalysis, and inspire further studies in this rapidly developing field.

catalytic, and environmental technologies. Several unique features of these materials are responsible for their success: uniform channels and cavities, active sites with different strengths, high adsorption capacity, and advantageous electronic properties. In general, crystalline porous materials include zeolites, ordered mesoporous silica, and metal–organic frameworks (MOFs). Although their common features endow these porous materials with many advantageous properties, their differences determine the advantages and disadvantages for particular applications, especially catalysis.

Zeolites represent a revolution of crystalline porous materials.^[1] They are an important group of heterogeneous catalysts with large-scale applications in the petroleum industry and an increasing application potential in environmental catalysis.^[2–6] Zeolites are crystalline alumi-

1. Introduction

Crystalline porous materials continuously attract scientific community interest due to their applications in petrochemical,

nosilicates with 3D four-connected frameworks built by corner sharing SiO₄ and AlO₄ units and a Si/Al ratio greater than one. Other atoms with tetrahedral coordination such as Ge, B, and Ti can also be introduced into the framework and enrich the zeolite family.^[1] Two hundred thirty-two types of zeolite frameworks are officially recognized by the Structure Commission of the International Zeolite Association (IZA-SC).^[7] These zeolite frameworks exhibit different size, shape, and connectivity of channels from 8 to 30 rings, with a maximum pore size of 0.74 nm (12-ring) for industrial applications.^[8–10] Due to their exceptional stability and limited pore size, zeolites have been used as heterogeneous catalysts under harsh conditions since the 1960s, soon after the first synthesis of these materials.^[11,12] Zeolite Y, ZSM-5, mordenite, beta and ferrierite are popular zeolites in industry due to their good performance and relatively economical production.^[13] However, they may be inadequate when processing reactants with molecular dimensions greater than their micropores.

The discovery of MCM-41 in the 1990s, a member of the M41S family characterized by ordered mesopores, created a new perspective for heterogeneous catalysis.^[14,15] Later, related mesoporous silica materials such as MCM-48, MCM-50, FSM-16, and SBA-15 were reported.^[16–20] These mesoporous materials have high surface areas (800–1400 m² g⁻¹), large pore volumes, and tunable pore dimensions (2–50 nm), which are of great interest for adsorption, catalysis and sensing.^[21–27] The relatively large pores in mesoporous silica facilitate mass transfer, and the high surface area allows for a high concentration of active

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DOI: 10.1002/adma.201701139

sites per mass of materials. Mesoporous silica enables catalytic reactions involving bulky substrates and/or products. Although mesoporous silica exhibits long-range ordering of regular mesopores, their surrounding walls are amorphous, in contrast to the crystallographically defined pore walls of zeolites. The amorphous nature of mesoporous silica implies that its stability and catalytic activity is inherently lower than those of zeolites. To overcome these limitations, innovative strategies were developed to synthesize microporous crystalline materials made of an ordered system of mesopores with crystalline microporous walls.^[28–33] The catalytic performance of the materials in several reactions was promising. For instance, mesostructured zeolites Y, mordenite, and ZSM-5 had interesting catalytic cracking results compared with their parent zeolites and MCM-41.^[34–36]

More recently, another class of porous material has gained the attention of scientists: MOFs. In contrast to the purely inorganic materials zeolites and mesoporous silica, MOFs are inorganic–organic materials constructed from inorganic nodes (metal ions or clusters) coordinated with organic linkers to form 3D coordination networks.^[37–43] Nearly all the transition metals and a large variety of organic linkers have been used in the synthesis of MOFs, resulting in thousands of frameworks that vary different in structure and composition.^[44,45] Among them, the largest surface area observed was up to 10 400 m² g^{−1} and the pores were from ≈0.5 to 9.8 nm.^[46,47] These attractive features give MOFs great potential for various applications such as heterogeneous catalysis. Several reviews on MOFs catalysis have been published, despite the relatively short time since the first catalytic application of MOFs was explored.^[48–59] However, it should be noted that the low thermal and chemical stability of major MOFs pose problems during catalytic reactions. This may explain why highly robust MOFs materials, such as MIL-101(Cr), UiO-66(Zr), PCN-224(Zr), and etc., are favored as catalysts.^[60–67]

As discussed above, all three types of porous materials (zeolites, mesoporous silica, and MOFs) are very attractive for catalytic applications. In this review, we aim to provide a comparison of the catalytic activities of zeolites, mesoporous silica, and MOFs. We first describe the distinctive structural, physical, and chemical properties of these porous materials to screen for suitable reactions from a catalytic perspective. Then, the catalytic behavior of zeolites, mesoporous silica, and MOFs in four types of general organic reactions (acid, base, oxidation and hydrogenation) is discussed. Particular attention is given to the advantages and disadvantages of these porous materials for particular catalytic reactions. The final section summarizes the main conclusions discusses the future development of the three types of porous materials in heterogeneous catalysis.

2. Comparison of the Structure and Catalytically Relevant Properties of Zeolites, Mesoporous Silica, and MOFs

2.1. Structural Relationships of Zeolites, Mesoporous Silica, and MOFs

Figure 1 shows the typical structural models of zeolites (zeolite Y, zeolite beta, ZSM-5), mesoporous silica (MCM-41, SBA-15),



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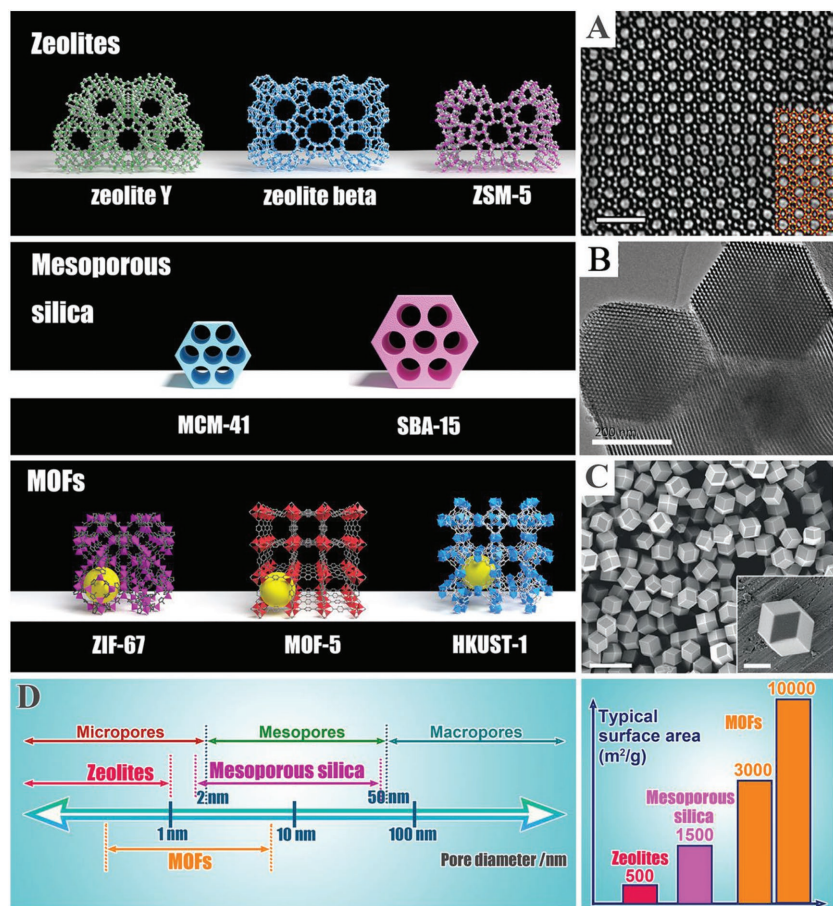


Figure 1. Upper left: Structural models of (top) zeolites (zeolite Y, zeolite beta, and ZSM-5),^a (middle) mesoporous silica (MCM-41 and SBA-15), and (bottom) MOFs materials (ZIF-67, MOF-5, and HKUST-1).^a Structures obtained from their single-crystal X-ray diffraction data. A) Bragg-filtered HR-TEM image of a zeolite. Reproduced with permission.^[68] Copyright 2015, Nature Publishing Group. B) TEM image of SBA-15. Reproduced with permission.^[69] Copyright 2017, Elsevier. C) SEM images of a Zn-based MOF. Reproduced with permission.^[70] Copyright 2015, Wiley-VCH. Scale bar: A) 3 nm, B) 200 nm, C) 2 μ m and 500 nm (inset in C). D) Schematics of pore diameters (left) and typical surface areas (right) of zeolites, mesoporous silica and MOFs.

and MOF materials (ZIF-67, MOF-5, HKUST-1). The characteristic structural features and properties of these porous materials are summarized in **Table 1**. Although zeolites, mesoporous silica, and MOFs share a number of catalytically relevant features such as large surface area, and uniform pores and voids, they also differ in several important aspects as discussed below.

Zeolites and MOFs are crystalline porous materials, whereas mesoporous silica has amorphous pore walls. The crystallinity of zeolites and MOFs allow for determination of the exact chemical composition and position of the atoms in space, whereas it is difficult to determine the fine structure of mesoporous silica. Due to the amorphous nature of mesoporous silica, the incorporation of heteroelements into mesoporous silica leads to a wide variety of different sites with different local environments rather than defined sites as in zeolites and MOFs. Consequently, the acidity of mesoporous silica is substantially weaker than that of zeolites. The amorphous nature of mesoporous silica also has important consequences on their properties, such as

low thermal and hydrothermal stability, due to the large concentration of silanol groups on the pore walls.

Second, there is a large difference in the pore size of these porous materials. Zeolites rarely have pore sizes larger than 1 nm without a significant loss in stability whereas mesoporous silica has pore sizes of 10 nm in some cases. Interestingly, MOFs may bridge the gap between zeolites and ordered mesoporous silica with pore dimensions from ultramicropore to mesopore. Their varying pore sizes make the three porous materials suitable for different catalytic reactions. For example, the size constraint of zeolites is advantageous in terms of shape selectivity although the diffusion of substrates is slow. In contrast, the large channels of mesoporous silica are beneficial for mass transport and could facilitate catalytic reactions involving bulky substrates and/or products although confinement effects can be difficult to impose on them. Consequently, the diffusivity of mesoporous silica and MOFs is higher than that of zeolites.

Third, the higher surface area of mesoporous silica and MOFs allows for a higher concentration of active sites per mass of material. One difference is that the distribution of active sites in mesoporous silica is normally inhomogeneous due to the amorphous walls whereas the periodicity and regularity of active sites in MOFs make them “single-site catalysts.” This is different from the homogeneous but random distribution of active sites in zeolites. The advantage of “single-site catalysts” is that all the active sites have the same environment and exhibit identical performance to achieve the maximum possible activity. Thus, MOFs provide a great

opportunity to rationally design the active site and the microenvironment with an unprecedented degree of precision.^[71]

Fourth, due to the large pore size and pore volume, mesoporous silica and MOFs can serve as supporting materials for active homogeneous catalysts, metal, or metal oxide nanoparticles, and organometallic complexes. Several metal-doped mesoporous silica complexes as heterogeneous catalysts have been reported, including Cr-MCM-41, CeO₂-silica, Ti-MCM-41, Ce-Fe-SBA-15, and silica-supported Pt and Rh nanoparticles.^[72–76] MOFs (typically MOF-5, HKUST-1, MIL, UiO, PCN, and zeolitic imidazole framework (ZIF)) that incorporate similar metal and metal oxide nanoparticles were also reported, which were typically used as catalysts for C–C couplings, oxidation, hydrogenation, cyanosilylation, and other reactions.^[58,77–80] When evaluating the catalytic behavior of these types of porous materials, two competing effects should be considered: the activity is proportional to the number of active sites, but an increase of the active functions may result

Table 1. Structural, physical, and chemical properties of zeolites, mesoporous silica, and MOFs. Some properties may vary from case to case.

Properties	Zeolites	Mesoporous silica	MOFs
Crystalline	Yes	Amorphous pore wall	Yes
Pore size	≤1 nm	2–50 nm	0.5–9.8 nm
Surface area	<700 m ² g ⁻¹	<2000 m ² g ⁻¹	<10 400 m ² g ⁻¹
Pore volume	0.1–0.5 cm ³	<1 cm ³	>1 cm ³
Diffusivity	Low	High	Low to high
Thermal stability	High	Medium	Low to medium
Chemical stability	High	Limited	Limited
Chemical versatility	Low	Medium to low	High
Metal site density	Low	Variable	High
Lewis acidity	High	Low	Low to medium
Brønsted acidity	Bridging Si(OH)/Al hydroxyl groups	Introduced by functional groups in the pore wall	Introduced by postsynthetic modifications or functional groups in the ligands
Basicity	Arise from the oxygen framework	Introduced by functional groups in the pore wall	Introduced by post-synthetic modifications or functional groups in the ligands
Chirality	Difficult to achieve	Easily obtained	Easily obtained

in increasing diffusional limitations. Although zeolites can act as hosts for small metal particles (Pt, Pd, Rh, etc.) and perform shape-selective hydrogenation and redox reactions, the number of guest species that can be introduced is limited by the small pore volume, which consequently restricts the strength of active sites formed on zeolites.

Stability (thermal and chemical) is one of the most important parameters in heterogeneous catalysis because it establishes what type of application the material is suitable for. Zeolites are known for their pronounced thermal and hydrothermal stability. Although the stability of zeolites varies by material depending on the Si/Al ratio and the ionic potential (Z/r)_{wt}, the high-silica zeolites are usually stable up to 800 °C or greater.^[81] Mesoporous silica exhibits good thermal stability and it is well established that increasing the wall thickness would effectively improve its thermal stability. However, the hydrothermal stability of mesoporous silica, however, is much lower than that of zeolites due to the high concentration of silanols on the wall and the lack of crystallinity. For example, mesoporous MCM-41 structure is completely lost upon exposure to air for three months even at room temperature.^[82] Compared with inorganic porous solids, the thermal and chemical stability of MOFs is rather low and it is mostly dependent on metal–ligand interactions. Most MOFs decompose below 300 °C, and some frameworks may even decompose with air, moisture, and solvents. In the case of MOF-5, a slight exposure of the activated form to air results in rapid deprivation of the crystallinity.^[83,84] Recently, it was observed that the use of hard metal ions (high valance metals such as Cr³⁺, Fe³⁺, and Zr⁴⁺) with hard bases containing donor atoms (O or N) generates thermally and chemically stable MOFs.^[85] For example, a series of Zr-based MOFs, including UiO-66, UiO-67, Nu-1000, PCN-221, PCN-222, PCN-223, PCN-224, etc. were found to be stable up to 350 °C and were stable in the presence of water and many organic solvents.^[61–67,86]

2.2. Zeolites, Mesoporous Silica, and MOFs as Heterogeneous Catalysts

Because of their unique structural, thermal, and chemical stability, zeolites are ideal heterogeneous catalysts for gas-phase reactions that are typically conducted at temperatures greater than 300 °C.^[11,12,87,88] Under harsh conditions, diffusion limitations are generally less important. Thus, gas-phase reactions are suited for volatile simple hydrocarbons, and zeolites are perfect candidates for these processes. Most of the current large-scale commercial processes in the petroleum refining and petrochemical industries use zeolite-based catalysts.^[89] Applications primarily involve epoxidation, condensation, acylation, and amination processes. After several catalytic cycles, heterogeneous catalysts may become deactivated due to the adsorption of products or byproducts or the formation of coke or heavier residual products. However, zeolites can easily be reactivated by combustion, pyrolysis or thermal treatments.

Compared with robust zeolites, mesoporous silica and MOFs with lower stability and unlimited pore size are more suited for liquid-phase reactions. In contrast with gas-phase reactions, liquid-phase reactions are typically performed at temperatures less than 200 °C, and the catalytic activity is controlled by the substrate and product diffusion inside the pore systems. These conditions are typically employed for the production of fine chemicals characterized by more complex, diverse low-volatility molecules with high added value.^[90–97] Thus, mesoporous silica and MOFs are optimal catalysts for the production of fine chemicals.^[98,99] The use of these two porous materials for liquid-phase catalysis is under intense investigation, with an aim of developing real industrial processes based on these materials. Recently, the advent of Zr/Hf-based MOFs with high thermal and chemical stability has enabled gas-phase reactions over MOFs or MOF-supported species.^[100–102] Although several Zr-MOFs have been investigated for the gas-phase catalysis such as the oxidation of CO to CO₂ under harsh conditions,

these investigations are in early stages and more improvements are needed.

In the next sections, we focus on comparison of the catalytic behavior of zeolites, mesoporous silica, and MOFs for several gas-phase and liquid-organic reactions, organized in four main sections (acid, base, oxidation, and reduction) based on the nature of the sites that promote the reactions. Cooperative catalysts that originate from incorporation of additional acid or metal functionalities into these porous materials are also involved.

3. Application of Zeolites, Mesoporous Silica, and MOFs in Typical Organic Reactions

3.1. Acid-Catalyzed Reactions

Several industrial processes are based on solid acid catalysts. The Lewis and Brønsted acidities are provided by different active centers. For zeolites and mesoporous silica, the Lewis acidity is related to the bi- or trivalent cations in the framework. For MOFs, it originates from the coordination positions without compromising with framework. The Brønsted acidity is provided by bridging the Si(OH)Al hydroxyl groups in zeolites and by functional groups ($-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{NR}_3^+$) present in mesoporous silica and MOFs. Generally, the number and strength of acid sites determine the catalytic activity of materials and the selectivity of the organic transformations.

The acidity of porous materials is generally characterized with Fourier transform infrared spectroscopy (FTIR) or thermogravimetry using various probe molecules such as pyridine and ammonia. When pyridine is used as the probe molecule, the presence of Lewis and Brønsted acid sites and their relative amount can be determined from the FTIR spectra. The number of Lewis acid sites can be evaluated from the integral intensity of the absorption band at 1450 cm^{-1} and the Brønsted acid sites are related to the absorption band at 1545 cm^{-1} . Based on the desorption temperature, the strength of these acid sites can also be determined. The higher the desorption temperature is, the higher is the strength of interaction between acid sites and probe molecules. These characterization techniques work well in zeolites and mesoporous silica. However, they are not appropriate for MOFs due to the limited thermal stability of MOFs and intense IR bonds of the organic ligand at approximately 1545 and 1450 cm^{-1} . Thus, the use of test reactions such as the rearrangement of ethylene acetal of 2-bromopropiophenone is an optional method for characterizing Brønsted and hard/soft Lewis acids in MOFs.^[103,104]

More than 100 industrial processes in oil refining and petrochemistry have been developed using solid acid catalysts.^[105] In this section, we describe some examples that illustrate the catalytic behavior of zeolites, mesoporous silica, and MOFs in these reactions.

3.1.1. Alkylation Reactions

Ethylbenzene, generally synthesized from the alkylation of benzene with ethylene, has a large-scale application for

the production of styrene monomer. Its worldwide capacity amounts to 20 million tons per year. The alkylation reaction was formerly carried out primarily in the presence of homogeneous Lewis acid catalysts such as AlCl_3 , supported phosphoric acid, and HF. Since the 1970s, the discovery of shape-selective acidic ZSM-5 zeolite for gas-phase alkylation of benzene and ethylene has been the basis for breakthrough technology in the field of aromatic alkylation reactions using solid acid catalysts.^[106] This process accounts for 90% of all new ethylbenzene processes installed since 1980.^[105] Another zeolite, MCM-22, was also found to be selective for the monoalkylated product. It decreases the benzene-to-ethylene ratio from 5 molar to 3 molar, reducing benzene recycle.^[106] The liquid-phase ethylbenzene process was introduced in the early 1990s based on a modified Y zeolite catalyst, which greatly minimizes the production of oligomers and xylenes and maximizes ethylbenzene formation.^[105–107]

Cumene is also produced from the alkylation of benzene with propylene. It is an intermediate for phenol and acetone production, and the worldwide capacity of this process is ≈ 8 million tons per year. The production of cumene by liquid-phase process from benzene and propylene is based on similarly zeolitic catalysts to those in the ethylbenzene process.^[108–111] Zeolites with large pores are preferred because they present no diffusional restrictions for cumene through the 12-ring pores. In principle, the zeolite catalysts should be active for the alkylation and transalkylation, inactive for propylene oligomerization, and stable to allow for a long operating cycle before the regeneration.^[105]

Mesoporous silica was also tested in the alkylation reactions as acid catalysts. For example, MCM-41 showed good catalytic activity in the alkylation of benzene to ethylbenzene but produced higher amount of polyalkylates than ZSM-5.^[112] In the alkylation of toluene with propylene to isopropyltoluenes (cymenes), MCM-41 also exhibited good catalytic activity, similar to that of zeolite beta, but gave lower cymene selectivity as a consequence of polyalkylate formation.^[113] This outcome may be due to the lack of shape selectivity of mesoporous silica and low transalkylation activity. These results indicate that the use of mesoporous silica shows no significant advantages over zeolites for reactions that require strong acid sites and shape selective properties.

3.1.2. Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) is one of the most important processes in oil refining (Figure 2A). In FCC processes, heavy oil fractions are transformed into the desired products (gasoline and diesel) that can further react by cracking (i.e., propylene and butene) or polycondensation (i.e., coke).^[114] This is a vapor-phase reaction that occurs via a carbonium ion mechanism. In 1962, zeolite Y brought a revolution in FCC because it can substantially increase the gasoline production.^[115–119] Zeolite Y was further improved because its acid site density (Si/Al ratio) can be finely tuned and its stability against steam dealumination can be increased by introducing rare-earth ions (Figure 2B). These improvements make zeolite Y exceptionally adaptable to the FCC process. Recently, new zeolites have been proposed for

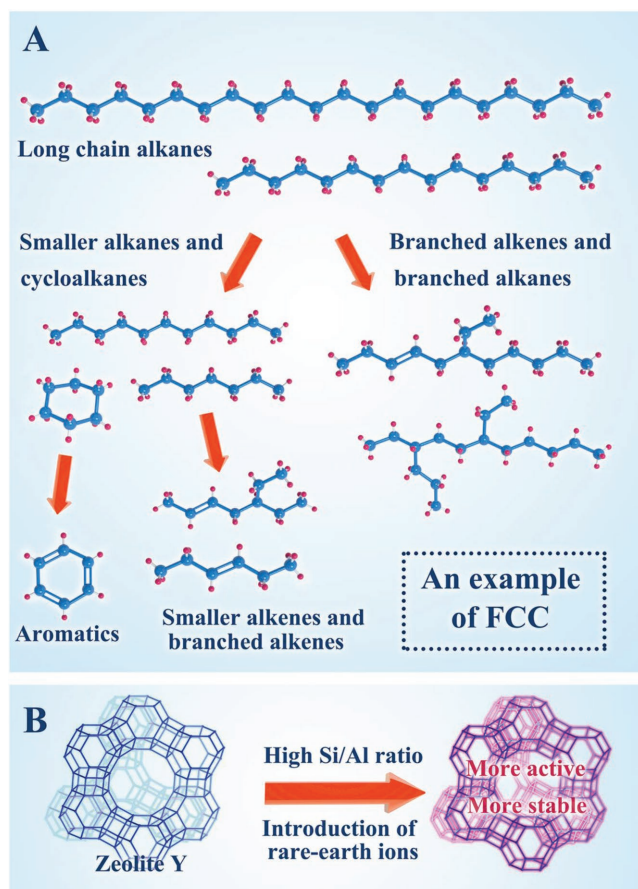


Figure 2. Fluid catalytic cracking. A) An example of FCC. B) Schematic of development strategies for zeolite Y for FCC catalysis.

FCC. ZSM-20 and ITQ-21, with a similar pore size as zeolite Y but with more open structure, produce higher amounts of diesel under FCC conditions.^[120–123] ITQ-33, with a 3D extra-large $18 \times 10 \times 10$ -ring channels, can increase the yields of propylene and diesel.^[124] Unfortunately, the application of these new zeolites is limited in practice due to their lower hydrothermal stability and high cost of synthesis. No other materials have been able to displace or have come close to displacing zeolite Y in the FCC process.

The cracking activity of mesoporous MCM-41 was investigated in cracking reactions performed on *n*-heptane, *n*-hexadecane, and 1,3,5-tri-isopropylbenzene (1,3,5-TIPB) in comparison with USY (zeolite Y in its ultrastabilized form).^[125,126] When cracking smaller *n*-heptane molecules, the catalytic activity of MCM-41 is much lower than that of USY due to fewer Brønsted acid sites with weaker strength in MCM-41. However, when the cracking reaction is performed on bulky molecules (*n*-hexadecane, 1,3,5-TIPB, and real FCC feedstock), MCM-41 shows higher conversion (95%) than H-Y (80%). This is predictable because zeolites have diffusion limitations for bulky molecules. Moreover, when using real FCC feedstock, MCM-41 is more selective than USY in the diesel formation, producing less gasoline but more coke. Thus, instead of aiming at replacing zeolite Y, the authors propose that MCM-41 be used as an active component of the matrix to pre-crack the bulky molecules,

enhancing the role of the zeolite as an FCC catalyst. This conclusion was further confirmed by Da et al. from Sinopec. They found that MCM-41-containing FCC catalyst (5 wt% MCM-41 and 30 wt% of REH-USY) is capable of cracking heavy oil feedstock, in which the yield of the diesel and lighter oil increased 1.85 and 3.47% respectively, and the yield of coke decreased 0.29%.^[127]

3.1.3. Oligomerization Processes

Oligomerization of alkenes to various homologues with a finite degree of polymerization plays a critical role in the oil refining industry, as it presents a synthetic route for producing useful oligomers such as liquid paraffin, plasticizers, and fuels. HZSM-5 zeolite has been extensively investigated for the oligomerization of light olefins including ethylene and propene.^[128–130] The catalytic behaviors of the zeolites for oligomerization greatly depend on the amount and type of their acid sites.^[131] At the outer edges of the catalysts, there are many Brønsted acid sites in the external edges of the zeolites, where the formation of highly branched oligomers are preferred, whereas the formation of linear oligomers is favored inside the zeolites. As a result, when the acid sites at the external walls of HZSM-5 were inactivated by amines, linear oligomers were primarily produced in the case of propene oligomerization.^[132–134] The same holds for zeolites with medium pores such as HZSM-22 and HZSM-35.^[135–138] Severe inactivation during the oligomerization process is a serious problem for most zeolites, mainly because the heavy compounds formed on the strong acid sites can block the micropores of the zeolites.^[139] In this regard, it is desirable that the zeolite catalysts possess larger pores and weaker acid sites and the oligomerization should be operated under mild conditions.

Due to its unique pore structure and acidity, mesoporous silica offers great opportunities for oligomerization of large olefins. Mesoporous silica exhibits prominent catalytic activities and selectivity toward gasoline or hydrocarbon. For example, in the presence of mesoporous silica alumina catalyst, the oligomerization of propylene mainly led to primarily gasoline and hydrocarbon with large molecular weights, and aromatics were not formed.^[140] The oligomerization reaction temperature required for mesoporous silica is normally much lower than that for zeolites due to the ordered open channels without much geometric limitation of mesoporous silica. The catalytic activity of mesoporous MTS-type aluminosilicates and acid zeolites (HBeta and HZSM-5) was compared in the oligomerization of butane at 150 °C and 14.7–19.6 atm.^[141] The acid zeolites were found to be inactive due to fast deactivation and low selectivity. In contrast, under the same conditions, the MTS catalyst was active and can selectively catalyze the oligomerization of butenes to various branched dimers. The catalytic activity of MTS catalyst can be ascribed to the small amount of the acid sites on the surface and the open channels that facilitate transport of the products.

Recently, MOF-based solid acid catalysts were also evaluated in the gas-phase oligomerization processes. One example is the oligomerization of propene catalyzed by Ni-MOF-74, in which the active sites are coordinatively unsaturated Ni ions present

on the nodes.^[142] Ni-MOF-74 shows similar activity for propene oligomerization to that of Ni-exchanged MCM-41 at 180 °C and 4.9 atm propene and has enhanced selectivity for the linear product. When the much higher content of acid sites per gram in Ni-MOF-74 is taken into account, Ni-exchanged MCM-41 is more active per acid site. Although the use of MOFs for gas-phase catalysis is in an early phase, the versatility of the pore structure and chemistry of MOFs provide great opportunities for designing new MOFs for catalysis of oligomerization of alkenes.

Although MOFs and mesoporous silica cannot compete with robust zeolite in gas-phase reactions, these materials are better suited for liquid-phase reactions conducted at moderate temperatures. These reaction conditions are typically employed for the production of fine chemicals with high added value that are characterized by more complex and diverse molecules of low volatility. In the following sections, we illustrate some heterogeneous reactions carried out in the liquid phase.

3.1.4. Friedel-Crafts Acylation

Friedel-Crafts acylation is a reaction to attach substituents onto aromatic rings and is one of the most important reactions in fine chemistry. This liquid-phase reaction is usually catalyzed by Lewis acidic centers and can be considered a model reaction that requires the presence of relatively strong acid sites in catalysts.^[143–145] Due to their tuned acidity, shape selectivity, and high stability, zeolite beta, and Y have been employed as acylation catalysts with substrates including xylenes (Table 2A), 2-methoxynaphthalene, anisole (methoxybenzene, Table 2B), and eratrole (1,2-dimethoxybenzene).^[146–151] The channel size and concentration of acid sites both influence of the conversion. The application of zeolite beta and Y in acylation of anisole and veratrole with acetic and anhydride was commercialized by the Rhodia company, showing the success of zeolites for acylation reactions.^[152] However, generalization of the process still requires improvements, particularly regarding rapid deactivation.

The MOFs Cu₃(BTC)₂, MIL-100(Fe), and MIL-100(Cr) were tested as catalysts in *p*-xylene acylation with benzoyl chloride and their catalytic behavior was compared with those of zeolite

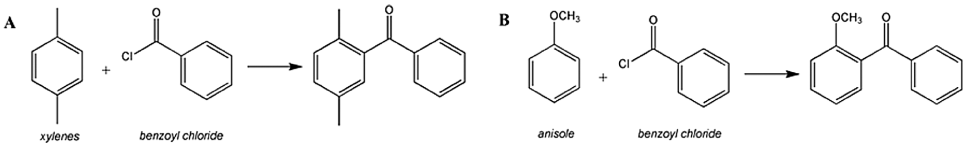
beta and Y (Table 2).^[153] Under similar reaction conditions, whereas zeolite beta and Y exhibited a similar conversion rate of 31% after 300 min reaction time at 130 °C, MIL-100(Cr) showed lower conversion rate of 20% and Cu₃(BTC)₂ gave slightly higher conversion of 37%. Surprisingly, MIL-100(Fe) exhibited the highest conversion of 100% within approximately 15 min of the reaction. The excellent performance of MIL-100(Fe) is assigned to the large amount of unsaturated Lewis acid sites connected with Fe, the wide pore windows (2.5–2.9 nm), and the optimal acid strength to interact with active substrates and to desorb the product. The selectivity to the target 2,5-dimethylbenzophenone was almost 100% for all tested zeolites and MOFs. Due to the mild reaction conditions, MIL-100(Fe) appears to be a more favorable acylation catalyst than conventional zeolites. However, the stability and reusability of MIL-100(Fe) after several catalytic cycles should also be determined because it is crucial for the evaluation of catalysts.

A mesoporous gallosilicate, GaSBA-15, also showed promising results in the acylation of anisole with benzoyl chloride when compared to zeolite BEA (Table 2).^[154] At 140 °C, a 98% conversion of benzoyl chloride was reached using GaSBA-15 after 24 h of reaction time with a selectivity of 92% toward the desired paramethoxybenzophenone. The GaSBA-15 catalyst was stable as a function of the cycling test because no deactivation was observed after each test due to its large pore size and moderate acidic character. In contrast, although zeolite BEA exhibited higher activity during the first test, a large deactivation was observed in the following tests. Thus, mesoporous SBA-15 doped with gallium can be efficiently employed as a catalyst in the Friedel-Crafts reaction with higher stability. The mesoporous gallosilicate GaSBA-15 was later coated on macroscopic host structures, e.g., carbon nanofiber composite, for directly testing in slurry bed reactions.^[155] However, for practical applications, special attention should be paid to the stability of active species after catalytic recycles.

3.1.5. Cycloaddition of CO₂ into Epoxides

Cycloaddition of CO₂ into epoxides (Figure 3A) is an important reaction for synthesizing value-added five-membered cyclic

Table 2. Friedel-Crafts acylation of (A) xylene and (B) anisole by benzoyl chloride catalyzed by different catalysts.



Catalysts	Substrate	Temperature [°C]	Time [h]	Conversion [%]	Selectivity [%]	Refs.
BEA	a	130	5	31	100	[153]
USY	a	130	5	46	100	[153]
Cu ₃ (BTC) ₂	a	130	5	37	100	[153]
MIL-100(Fe)	a	130	0.25	100	100	[153]
MIL-100(Cr)	a	130	5	20	100	[153]
GaSBA-15	b	140	24	98	92	[154]

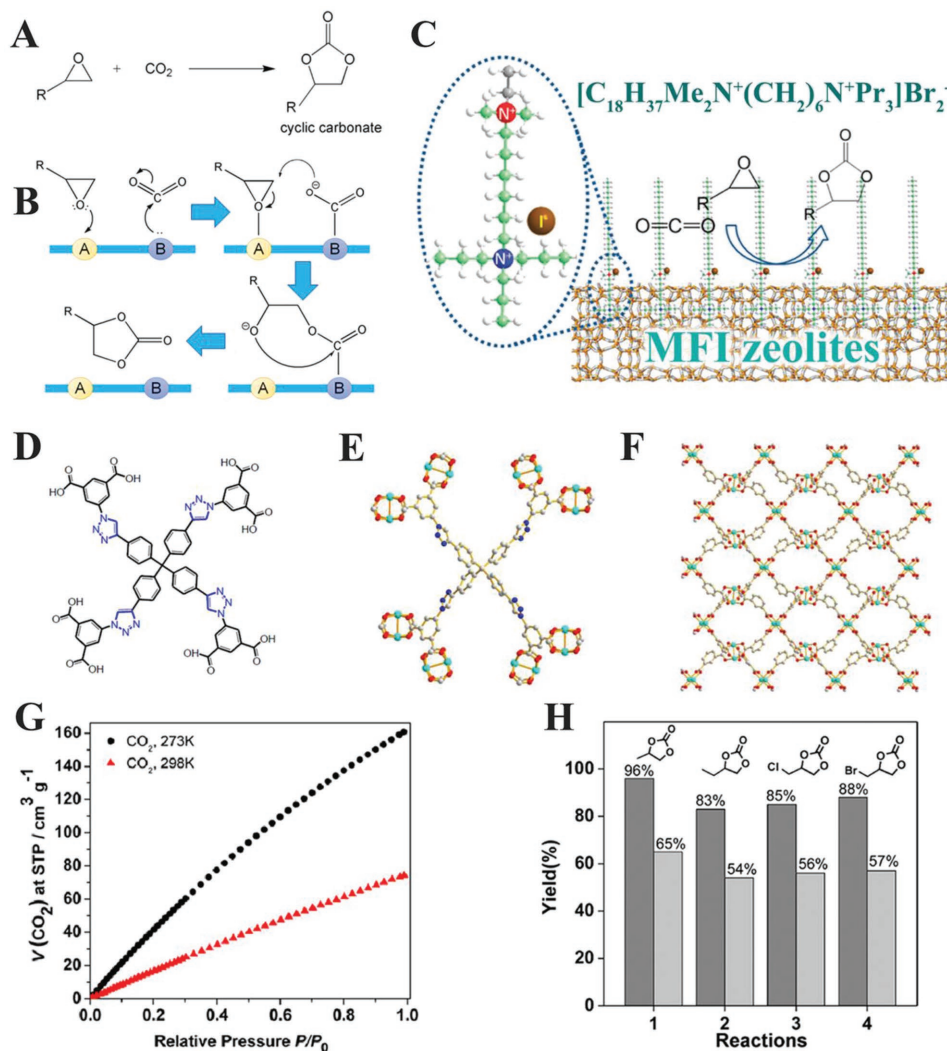


Figure 3. Cycloaddition of CO_2 to epoxides. A) Cycloaddition of CO_2 to epoxides. B) Proposed reaction mechanism using a catalyst with acid-base pairs (A, acid; B, base). C) Cycloaddition of epoxides and CO_2 over $[\text{C}_{18}\text{H}_{37}\text{Me}_2\text{N}^+(\text{CH}_2)_6\text{N}^+\text{Pr}_3]\text{Br}_2^-$ in lamellar MFI zeolites. Reproduced with permission.^[164] Copyright 2014, Royal Society of Chemistry. D) Ligand of MOF $\text{Cu}_4[(\text{C}_{57}\text{H}_{32}\text{N}_{12})(\text{COO})_8]$. E) Coordination of clicked octacarboxylate ligand and unsaturated paddlewheel Cu_2 units. F) Lamellar framework with regularly located Cu_2 sites connected by isophthalate moieties. G) CO_2 adsorption isotherms of MOF $\text{Cu}_4[(\text{C}_{57}\text{H}_{32}\text{N}_{12})(\text{COO})_8]$ at 0 and 25 °C, respectively. H) Yields of various cyclic carbonates prepared from the cycloaddition of CO_2 with related epoxides catalyzed by MOF $\text{Cu}_4[(\text{C}_{57}\text{H}_{32}\text{N}_{12})(\text{COO})_8]$ (black) and HKUST-1 (gray). The reaction was conducted in a Schlenk tube using epoxide (20 mmol) with CO_2 purged at 1 atm under a solvent-free environment at room temperature, catalyzed by 0.2 mol% per copper paddlewheel unit of MOF with a cocatalyst of tetra-*n*-tertbutylammonium bromide (0.65 g, 10 mol%) for 48 h. Reproduced with permission.^[166] Copyright 2016, American Chemical Society.

carbonates, which are widely used in pharmaceuticals, polymer industry, and biomedical fine chemical synthesis.^[156] It is also expected to be an effective method for reducing CO_2 emission.^[157] Both Lewis acid and base sites are necessary in the process: CO_2 is activated on the basic sites, forming a carbamate, that reacts with epoxides that are adsorbed on the acidic sites (Figure 3B).^[158–162] Although zeolites have a preponderance of acid sites, few base sites limit their application in the reaction of epoxide and CO_2 to produce cyclic carbonates. Among the few cases, it was observed that the catalytic activity of alkali-metal-modified zeolites increases as the basicity of these materials increases.^[163] Quaternary ammonium salts located in the channels of zeolites as templates can also facilitate the catalytic process, such as $[\text{C}_{18}\text{H}_{37}\text{Me}_2\text{N}^+(\text{CH}_2)_6\text{N}^+\text{Pr}_3]\text{Br}_2^-$ in lamellar MFI

zeolites (Figure 3C).^[164] Table 3 lists examples of several typical catalysts and references from the literature.

MOFs have been widely explored as catalysts in the cycloaddition of CO_2 to epoxides. Approximately 20 MOFs and their derivatives have been reported to catalyze this type of reaction. ZIF-8 was the first ZIF used as a catalyst for CO_2 cycloaddition to epichlorohydrin. Due to the Lewis acidic Zn center and the N basic moieties, ZIF-8 produced chloropropylene carbonate with a 44% yield at 80 °C and 6.86 atm of CO_2 and the selectivity to cyclic carbonate was 52%.^[165] The functionalized ZIF-8 with ethylene diamine improved the yield and the selectivity of the carbonate (73% and 73%) under similar conditions.^[165] This improvement is attributed to the high affinity of ethylene diamine for CO_2 .

Table 3. Conditions for CO₂ insertion into epoxides leading to OCs for several typical catalysts.

Catalysts	Substrate	Temperature [°C]	Pressure [atm]	Time [h]	Yield [%]	Refs.
NaX	–	150	100	3	1.4	[163]
KX	–	150	100	3	20.9	[163]
CsX	–	150	100	3	26.6	[163]
MFI	R=Cl–CH ₂ –	140	19.6	4	85.6	[164]
ZIF-8	R=Cl–CH ₂ –	80	6.86	4	44	[165]
NR ₂ -ZIF-8	R=Cl–CH ₂ –	80	6.86	4	73	[165]
Cu ₄ [(C ₅₇ H ₃₂ N ₁₂) (COO) ₈]	R=Cl–CH ₂ –	25	1	48	85	[166]
Cr-MIL-101	R=Ph–	25	7.84	48	95	[168,169]
Fe-MIL-101	R=Ph–	25	7.84	48	93	[168,169]
Ti-SBA-15	R=Cl–CH ₂ –	120	6.67	4	93.9	[170]

Similar results were found in our recently reported MOF Cu₄[(C₅₇H₃₂N₁₂) (COO)₈], which incorporates clicked octacarboxylate ligand and Cu(II) ions.^[166] Due to exposed Lewis-acid Cu(II) sites and accessible N-rich triazole groups, this MOF shows a CO₂ uptake of up to 160.8 cm³ g⁻¹ at 0 °C and 1 atm. As a result, the MOF acts as an efficient catalyst for CO₂ cycloaddition with small epoxides, with a yield of 96% for 2-methyloxirane, 83% for 2-ethyloxirane, 85% for 2-(chloromethyl)oxirane, and 88% for 2-(bromomethyl)oxirane under 1 atm CO₂ pressure and at room temperature for 48 h (Figure 3D–H). In contrast, the pore size excludes the entrance of large substrates such as 1,2-epoxyoctane, 1,2-epoxydodecane, and 2-ethylhexylglycidyl ether. For MOFs that lack basic sites, quaternary ammonium salts that act as co-catalysts are required for the cycloaddition of CO₂ to epoxides. For example, the addition of *n*-Pr₄NBr or *n*-Bu₄NBr into MOF-5 exerts a synergetic effect in promoting the cycloaddition of CO₂ into propylene oxide.^[167] *n*-Bu₄NBr also works well with Cr-MIL-101 and Fe-MIL-101 in the catalytic reaction.^[168,169] Although several MOFs are effective heterogeneous catalysts for the reaction of epoxides with CO₂ under mild conditions, the catalytic activity of most of these MOFs tends to decrease after several cycles on account of structural loss or blockage of the pores.

Weakly acidic Si–OH bonds in mesoporous silica hinder its application as a catalyst in cycloaddition reactions. However, this is not true if Lewis-acid sites (Ti) are used. Srivastava et al. investigated the catalytic activity of organic amine (propylamine and adenine)-immobilized SBA-15 and Ti-SBA-15 for CO₂ cycloaddition under solvent-free conditions.^[170] They suggested that, whereas the CO₂ molecule is activated on the basic nitrogen groups of adenine, epoxide is active on Lewis acidic Ti⁴⁺ ions. Thus, the increase in Ti content and surface concentration of the activated CO₂ species could lead to high catalytic activity. A recycling test indicates that some heavy carbonaceous products accumulate on the catalyst surface and result in the deactivation. However, initial activity could be restored after washing the deactivated catalyst with organic solvents.

3.1.6. Ring Opening of Epoxides

Ring opening of epoxides with nucleophilic reagents such as amines and alcohols is one of the most useful reactions in the chemical industry for producing bifunctional molecules (Figure 4).^[171] This reaction can be catalyzed by Lewis or

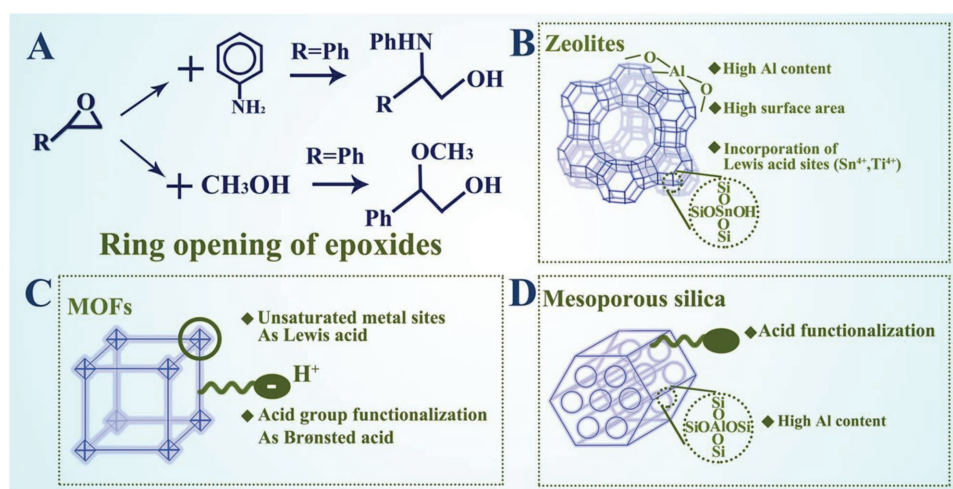


Figure 4. Ring opening of epoxides. A) Ring opening of epoxides with aniline or methanol. B–D) Schematic of development strategies of zeolites, MOFs and mesoporous silica for ring opening of epoxide catalysis.

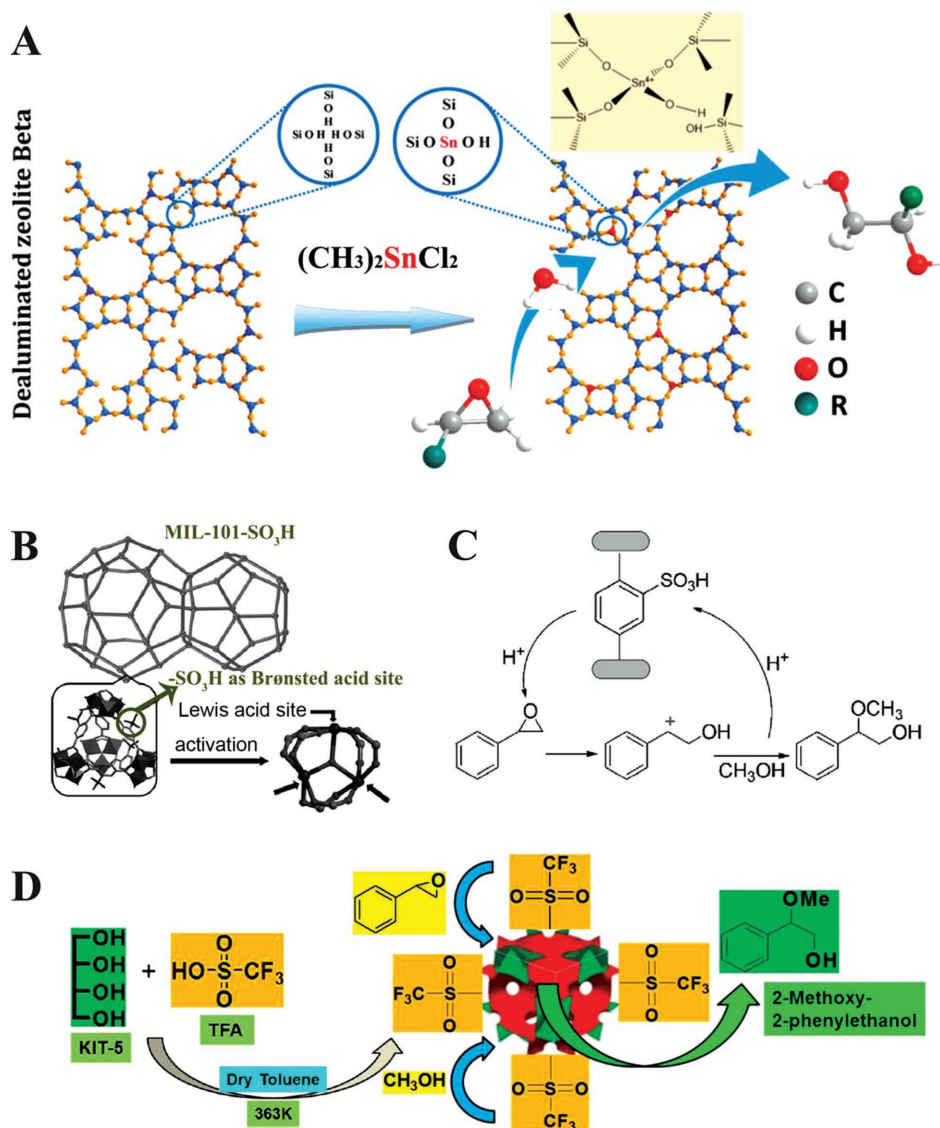


Figure 5. Ring opening of epoxides. A) Schematic representation of the incorporation of tetrahedrally coordinated Sn(IV) species into dealuminated zeolite beta. Reproduced with permission.^[174] Copyright 2014, American Chemical Society. B) Schematic illustration of the two types of cages in MIL-101-SO₃H with -SO₃H groups as Brønsted acid sites and open metal sites as Brønsted and Lewis acid sites, respectively. C) Proposed mechanism for the ring opening of styrene oxide in MeOH catalyzed by the Brønsted acid sites in MIL-101-SO₃H. Reproduced with permission.^[177] Copyright 2014, Wiley-VCH. D) Functionalization of triflic acid into KIT-5 mesoporous materials. Reproduced with permission.^[182] Copyright 2016, Wiley-VCH.

Brønsted acids in the presence or absence of solvents. For this process to be of synthetic use, the epoxide ring opening should be performed under mild conditions with high regioselectivity towards the desired products.

Several zeolites, zeolite 4A, zeolite 5A, zeolite X, Na-beta, NaY, Na mordenite, and ZSM-5, were tested as catalysts for ring opening of epoxides (styrene and propene) with aniline under solvent-free conditions.^[172] It was observed that the catalytic activity correlates with the Lewis acidity (aluminum content) and surface area. Among the zeolites tested, zeolite NaY, with high aluminum content and surface area, is most active for the reaction. An excellent yield of 92% and regioselectivity of 100% toward β -amino alcohol were achieved in 6–10 h reaction time at room temperature. In contrast, zeolite Na mordenite, with

low surface and low aluminum content, was found to be a poor catalyst.^[172] It was noted that, under microwave irradiation, an excellent yield of β -amino alcohol up to 94% can be achieved in 2.5 min with NaY as the catalyst (80 times faster than the reaction conducted at room temperature).^[173] Incorporating metal ions (Sn⁴⁺, Zr⁴⁺, and Ti⁴⁺) in the BEA framework is an effective method to improve its catalytic activity in epoxide hydration (Figure 5A). The catalytic activity correlates with the Lewis acid strength of the metal-containing zeolites in the sequence of Sn-beta > Zr-beta > Ti-beta.^[174] The stronger is the Lewis acid employed, the more efficiently the substrate molecules are activated on the acid sites and the higher is the catalytic activity that can be achieved. Sn-beta exhibits a distinctly high conversion (90.2%) and high 1,2-diol selectivity (92.7%) in ring

opening of cyclohexene oxide at near-ambient and solvent-free conditions in 6 h.

For ring opening of epoxides with alcohols, acid zeolites are generally not good catalysts because they are prone to adsorb methanol rather than the substrates and alcohols will neutralize the acid sites of the acid zeolites, reducing their acid strength. Several MOFs have been investigated as catalysts in ring opening of epoxides with alcohols. Fe(BTC), with one coordination position of Fe³⁺ occupied by a solvent molecule, behaves as a strong Lewis acid and was reported to be an efficient heterogeneous catalyst for regioselective ring opening of styrene oxide with methanol.^[175] The conversion and selectivity toward the formation of 2-methoxy-2-phenylethanol are 99% and 94%, respectively. A recycling test confirmed that Fe(BTC) can be reused three times before deactivation, making it a true heterogeneous catalyst. The analogous compound Cu₃(BTC)₂ was also found to be effective, although with somewhat lower activity than Fe(BTC).^[175] The much lower activity of Al₂(BDC)₃ than Fe(BTC) and Cu₃(BTC)₂ is due to its fully coordinated Al³⁺ ion by BDC linkers, which cannot act as a Lewis acid.^[175] A recently reported MOF Eu(Hpmd)(H₂O) was also employed in the methanolysis of styrene oxide at 55 °C.^[176] It was observed that the crystal size plays a determinant role in the catalytic process. Whereas microcrystalline MOF does not possess significant catalytic activity, its nanosized counterpart exhibits relatively high catalytic activity and excellent selectivity towards 2-methoxy-2-phenylethanol (100% yield within 48 h). A sulfonic acid group-functionalized MOF, MIL-101-SO₃H, was the first MOF material to catalyze ring opening of epoxides with Brønsted acid sites (Figure 5B,C).^[177] Under ambient conditions, ≈100% conversion and 100% selectivity can be achieved in ring opening of styrene oxides with methanol in 30 min. Notably, the catalytic performance of MIL-101-SO₃H far exceeds all previously reported Lewis acid-type MOF catalysts for ring opening of styrene oxide in methanol. Asymmetric ring opening reactions of epoxides are also realizable in the presence of chiral MOFs catalysts. For example, Shiro and co-workers successfully synthesized a Cu-based chiral MOF using chiral 2,2'-dihydroxy-1,1'-binaphthalene-5,5'-dicarboxylic acid as a ligand, which can enantioselectively catalyze the ring opening of a broad range of epoxides with various amines into β-amino alcohols with optical activity without the use of solvent.^[178]

Different metal ion complex or acid incorporated mesoporous silica has also been reported for ring opening of epoxides.^[179–182] Among these, a triflic acid-functionalized mesoporous silica KIT-5 (denoted as KIT5-FTA, Figure 5D) with a 3D cage-like framework was reported to complete ring opening of styrene oxides with methanol in 20 min at room temperature due to higher acidity of the catalyst.^[182] Under similar conditions, the catalytic activity of Al-incorporated KIT5-FTA is higher than those of SBA-15 and MCM-41. This is attributed to the higher total acidities of Al-incorporated KIT5-FTA (0.50 mmol g⁻¹) than those of SBA-15 and MCM-41 (0.44 and 0.36 mmol g⁻¹) and its unique 3D cage-like framework that can incorporate more Al species.^[183–185] When other alcohols were tested, KIT5-FTA also provided high yields of 95%, 94% and 90% for primary, secondary, and tertiary butyl alcohols, respectively. The slightly decreased yield from primary to secondary to tertiary alcohols is mainly due to the increase in steric hindrance.

3.2. Base-Catalyzed Reactions

The basicity in a matrix is always related to its acidity. In zeolites, because the protons and the exchangeable cations are the acid sites, the oxygens of the framework are the basic sites. In the same manner, –NH₂, –NMe₂, and –COO⁻ groups account for the Lewis and Brønsted basicity in mesoporous silica. The basicity in MOFs is introduced by postsynthetic modifications or functional groups such as –NH₂, pyridyl, and amide groups in organic linkers. The characterization of the basic properties is different among these porous materials. For zeolites and mesoporous silica, acid probe molecules such as pyrrole, CO₂, methanol, methyl iodide, and N₂O₄ are adsorbed on the materials and spectral changes are recorded to gain insight into the surface basicity, especially the nature and strength of basic sites. For pyrrole adsorption on alkaline zeolites, the frequency shift of IR NH-stretching vibration is employed to monitor the basic strength of the framework oxygen. The smaller of the frequency shift, the weaker the basic strength. The band intensity further suggests the relative density of basic sites in alkaline zeolites. However, test reactions such as Knoevenagel condensation are needed to characterize the basicity of MOFs. Knoevenagel condensation of aldehydes with active methylene compounds having two electron withdrawing groups is one of the most important C–C bond forming reactions (Figure 6).^[186,187] This reaction is a convenient approach to obtain α,β-conjugated esters and nitriles. In addition to the target products, some by-products caused by side reactions such as like self-condensation and oligomerization may result. On account of the amenable reaction conditions and analysis, Knoevenagel condensation is a preferred model reaction to evaluate the basicity of solid catalysts. The catalytic activities in Knoevenagel condensation over several porous materials are listed in Table 4.

In zeolites, negative framework oxygens generate base strength between that of MgO and NaOH. Thus, zeolites are able to catalyze reactions that require weak and medium basic strength. Zeolites X and Y exchanged with alkali metal cations are active and selective catalysts for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.^[186] Because the catalytic activity increases with the framework Al content and with the radius of the counter cation, CsX zeolite acts as the most active basic catalyst and exhibits the maximum basic strength. Other metal exchanged zeolites such as Zn exchanged beta zeolite, also exhibit higher yield (73%) than its H forms (65%) due to good coordination with aldehyde and active methylene compounds at 140 °C under solvent-free conditions.^[188] In sharp contrast with acidic zeolites, basic zeolite catalysts have seldom been applied in industrial applications. One important handicap is that inexpensive KOH and NaOH are their competing catalysts. The low cost and easy processing of the formed residues reduce the possibility of zeolite application to cases in which special selectivity is needed.

Mesoporous silica seldom shows any basic properties and the introduction of basic compounds (amines, ion liquids, and alkali earth metal oxides) is required. Amines are frequently chosen to be covalently bonded to the silica surface to increase the base strength. Aminopropyl-functionalized SBA-15 exhibits a yield of 99% for Knoevenagel condensation of ethyl cyanoacetate and benzaldehyde at 82 °C in 1 h.^[189] An acid–base

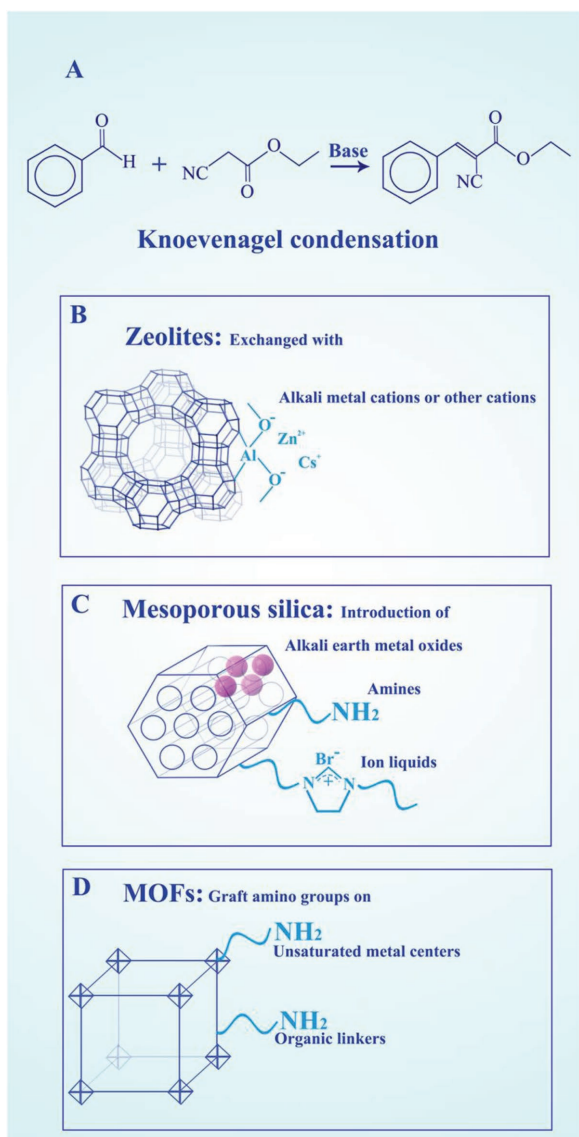


Figure 6. Knoevenagel condensation. A) Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. B–D) Schematic of development strategies of zeolites, mesoporous silica and MOFs for Knoevenagel condensation.

bifunctionalized mesoporous silica $NH_2-SO_3H-MCM-41$ catalyst shows high activity in the one-pot deacetalization Knoevenagel reaction to produce benzylidene ethylcyanoacetate

Table 4. Catalytic activities in Knoevenagel condensation over several typical catalysts.

Catalysts	Temperature [°C]	Time [h]	Solvents	Yield [%]	Refs.
CsX	140	2	Solvent free	67	[186]
Zn-beta	140	6	Solvent free	73	[188]
H-beta	140	6	Solvent free	65	[188]
$NH_2-SBA-15$	82	1	Solvent free	99	[189]
ED-MIL-101(Cr)	80	19	Cyclohexane	98	[193]
$NH_2-IRMOF-3$	40	2	DMSO	99	[194]

from ethylcyanoacetate with benzaldehyde dimethylacetate (Figure 7A,B).^[190] Basic ionic liquid and inorganic species can also be introduced to mesoporous silica to increase the base strength. Ionic liquid immobilized mesoporous silica has better reusability than amino-functionalized mesoporous silica. For instance, in Knoevenagel condensation of benzaldehyde with malononitrile, ionic liquid immobilized MCM-41 shows a high yield of 85% even after reusing it ten times. In contrast, the yield of benzylidene malononitrile by amino-functionalized MCM-41 declined from 97% to 74% after six recycles. This is ascribed to the lower leaching level of ionic liquid immobilized MCM-41 (5%) than that of amino-functionalized MCM-41 (16%–18%).^[191] MgO-incorporated MCM-41, MgO/MCM-41, shows a yield of 93.3% in condensation of benzaldehyde and malononitrile at 80 °C after reaction for 4 h.^[192]

Regarding MOFs, the metal nodes and organic linkers should be modified by functional groups to introduce the basicity. For example, ethylenediamine grafted on the coordinatively unsaturated metal sites of MIL-101(Cr) leads to better catalytic performance (98% conversion and 99% selectivity towards ethyl trans- α -cyanocinnamate) than that of dehydrated MIL-101(Cr) (32% conversion) for condensation of benzaldehyde with ethyl cyanoacetate at 80 °C.^[193] Another amino-functionalized IRMOF-3 exhibits a yield of 99% and selectivity of 100% to the condensation product in Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate in DMSO.^[194] The authors claimed that IRMOF-3 is more active than other basic catalysts, including zeolite and functionalized mesoporous silica. Other factors (e.g., solvent, catalyst dosage, and temperature) may also play roles in the catalytic activity, which should be considered when comparing different catalysts. An acid–base bifunctionalized MOF, PCN-124, similar to the abovementioned mesoporous silica $NH_2-SO_3H-MCM-41$, also shows high catalytic activity in deacetalization–Knoevenagel condensation of benzaldehyde with malononitrile (Figure 7C–F).^[195] Whereas the basicity originates from amide groups in PCN-124, weakly Lewis acidity comes from open Cu paddlewheel motifs. Thus, in contrast to zeolites, mesoporous silica and MOFs offer high potential for embedding various active sites, implementing multifunctional catalysis and enabling development of tandem reactions. However, no basic sites stronger than amines (such as nucleophilic organocatalysts and alkali earth metal oxides) have been introduced into MOFs, probably due to structural collapse under basic conditions. The low basicity confines the applications of amine-modified MOFs in Knoevenagel condensation reactions.

3.3. Oxidation Reactions

The redox property of porous materials is always endowed by transition metals (e.g., Ti^{4+} , V^{4+} , Sn^{4+} , Zr^{4+} , Fe^{3+} , Co^{3+} , Mn^{4+} , and Cu^{2+}) in the frameworks. Compared with MOFs having a high content of transition metals as convenient oxidation sites, zeolites and mesoporous silica are devoid of activity for oxidation reactions and transition metals are grafted on the framework to introduce the redox property. Transition metals can be introduced to occupy the framework or extra-framework positions in zeolites and mesoporous silica. Hence, the metal

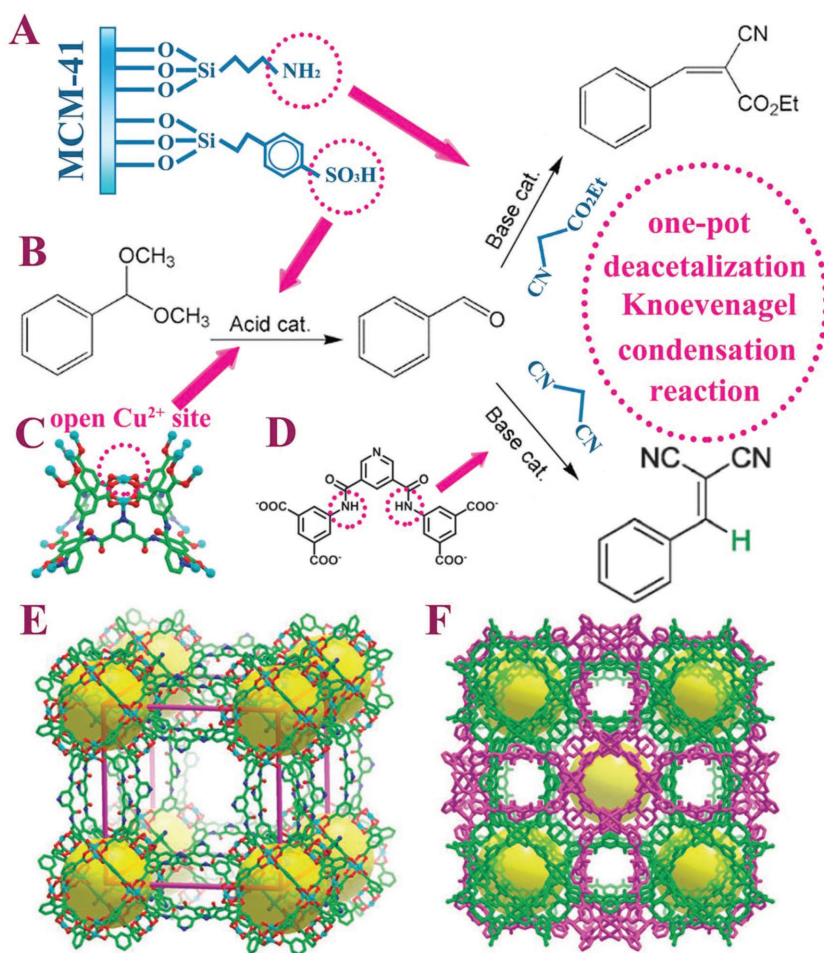


Figure 7. One-pot deacetalization Knoevenagel condensation reaction. A) Acid–base bifunctionalized mesoporous silica. B) Deacetalization–Knoevenagel reaction. C) Coordination environment of the dinuclear Cu paddlewheel motifs and ligands in PCN-124. D) Linker of PCN-124. E) A single cubic framework of PCN-124 constructed by ligand skeletons bridging molecular building block cages (Cu atoms are shown in cyan, O atoms in red, N atoms in blue, C atoms in green). F) Self-interpenetrated structure of PCN-124. Reproduced with permission.^[195] Copyright 2012, Royal Society of Chemistry.

content is lower in transition metal-containing zeolites and mesoporous silica (<2 wt%) than that in MOFs ($\approx 20\%$).

Titanosilicate zeolites have shown excellent catalytic performance in oxidation reactions over other metallosilicate. TS-1 (Ti-silicate, **Figure 8A**) is proven to be an efficient catalyst for liquid-phase oxidation of various organic compounds using H_2O_2 as an oxidant, and several industrial processes (e.g., ammoximation of cyclohexanone, propylene epoxidation, and hydroxylation of phenol) are operated using TS-1.^[196] The ammoximation of cyclohexanone to cyclohexanone oxime, catalyzed by TS-1, is conducted in liquid phase in the presence of ammonia and H_2O_2 (**Figure 8D**).^[197,198] This is an important route to produce ϵ -caprolactam, an intermediate for the production of Nylon-6. Almost complete conversion of cyclohexanone and up to 99% selectivity to oxime were reported at 80 °C with *t*-butanol as the solvents.^[199] Good results were also reported in co-solvent free condition.^[200] A key feature of TS-1 catalysts is their relatively high hydrophobicity, leading to favorable adsorp-

tion of hydrocarbons. After the success of TS-1 as a liquid-phase oxidation catalyst, efforts have been devoted to the synthesis of other Ti-containing zeolites, such as TS-2, Ti-beta, Ti-MOR, and Ti-MWW.^[201–207] Their catalytic behavior was also studied under similar conditions as those of TS-1. Notably, Ti-MWW exhibits superior catalytic performance over TS-1, with 99% selectivity and 99% conversion of ketone under optimized conditions.

Although Ti-containing zeolites are active in the reaction of small substrates, they are not as efficient when large hydrocarbons are employed as substrates with *tert*-butylhydroperoxide (TBHP) as the oxidant due to relatively small pores with a diffusion issue. This problem could be solved using Ti-containing mesoporous silica materials such as Ti-containing MCM-41, SBA-15, and MTS-9. For example, in oxidation of α -terpineol using TBHP as an oxidant, Ti-MCM-41 shows higher alkene conversion (62.2%) and epoxide selectivity (30.2%) than Ti-beta zeolite (32.7% and 12.8%, respectively).^[208] In another case, the mesoporous titanosilicate MTS-9, synthesized by assembly of preformed TS-1 nanoclusters into an ordered mesoporous structure, shows activity and selectivity similar to those of TS-1 in styrene epoxidation (**Figure 8B,C,E**). In 2,3,6-trimethylphenol (which has a large diameter and is inaccessible to the small micropores of TS-1) hydroxylation, MTS-9 exhibits a higher conversion of 18.8% and selectivity of 66.7% toward trimethylhydroquinone at 80 °C after 4 h than TS-1 and Ti-MCM-41.^[209] The higher catalytic activity of MTS-9 is due to its large pore diameter and its TS-1-like environment of Ti. Silanized Ti-MCM-41 in combination with TBHP is a good catalyst for epoxidation

of propene.^[210] Silanization is to expel water from the interior of mesoporous silica, to reduce the hydrophilicity of MCM-41, and to increase the selectivity towards epoxide. Notably, although these reported mesoporous titanosilicates have advantages for oxidation of bulky alkenes, none are intrinsically more active than TS-1 in reaction of small substrates in which the pore diffusion is not a problem.

Different from zeolites, mesoporous silica is advantageous in working as host matrix to support transition metal nanoparticles with high dispersion. This further facilitates their use as catalysts in oxidation reactions. For example, in vapor-phase epoxidation of propylene using H_2 and O_2 over Au-supported Ti-MCM-41 (**Figure 9A**), a maximum propylene conversion of 3.2% and propylene oxide selectivity of 93.5% were achieved at 100 °C.^[211] In gas-phase oxidation of cyclohexanol to cyclohexanone, mesoporous silica EP-FDU-12-supported Au nanoparticles exhibited good catalytic activity and high selectivity (>99.5%) at temperatures between 180 and 250 °C. The Au

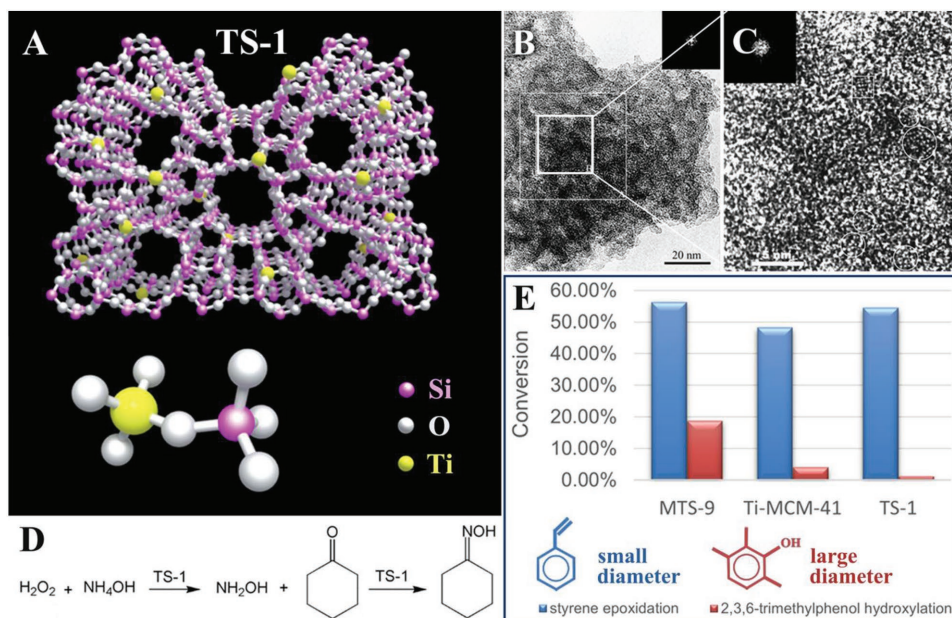


Figure 8. Oxidation reaction. A) Structural model of TS-1. D) Ammoxidation of cyclohexanone catalyzed by TS-1 in the presence of H_2O_2 and NH_4OH . B) TEM images of MTS-9. C) TEM image of MTS-9 with high magnification from selected region in (B). Areas of ordered micropore arrays are circled. Reproduced with permission.^[209] Copyright 2002, American Chemical Society. E) Catalytic activities in oxidation reactions by H_2O_2 over MTS-9, Ti-MCM-41, and TS-1 samples. In styrene epoxidation, with acetone as a solvent, $T = 45\text{ }^\circ\text{C}$, styrene/ $H_2O_2 = 3/1$ (molar ratio), $t = 5$ h, catalyst/phenol = 5% (weight ratio). In the 2,3,6-trimethylphenol hydroxylation, acetonitrile as a solvent, $T = 80\text{ }^\circ\text{C}$, trimethylphenol/ $H_2O_2 = 3/1$ (molar ratio), $t = 4$ h, catalyst/phenol = 5% (weight ratio).

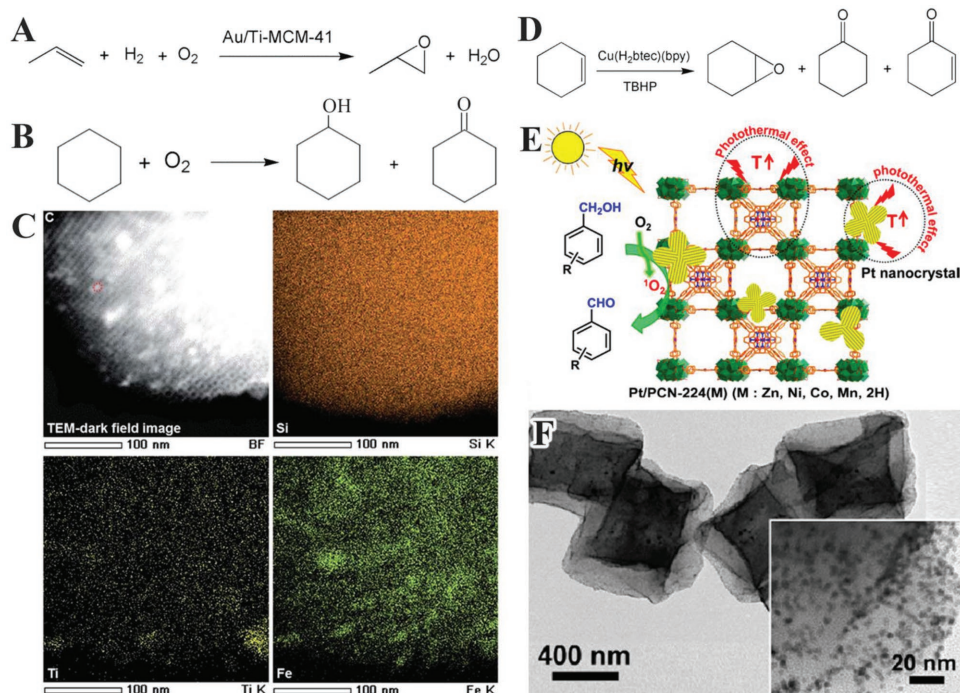


Figure 9. Oxidation reaction. A) Epoxidation of propylene over Au-supported Ti-MCM-41 in the presence of H_2 and O_2 . B) Partial cyclohexane oxidation with O_2 as the oxidant. C) TEM dark field image and EDX elemental mappings of SBA-15 with grafted Ti and Fe_2O_3 nanoparticles. Reproduced with permission.^[214] Copyright 2016, Royal Society of Chemistry. D) Oxidation of cyclohexene over $[Cu(H_2btec)(bipy)]$. E) Schematic illustration showing the singlet oxygen-engaged selective oxidation of alcohols over Pt/PCN-224(M) using molecular oxygen under visible-light irradiation. F) TEM and enlarged TEM images of Pt/PCN-224(Zn). Reproduced with permission.^[218] Copyright 2017, American Chemical Society.

nanoparticles encapsulated in the extra-large spherical cages of EP-FDU-12 afforded a long lifetime (>500 h) without poisonous coke formation and obvious mass-specific activity loss.^[212] Several Pt, Pd, Rh, and Au nanoparticles on mesoporous silica CMI-1 supports were tested as catalysts for *n*-butanol oxidation. The results showed that the Pt-based catalyst exhibited the highest catalytic activity, which was influenced by the particle size and surface area of the support. The activity of Pt/CMI-1 was followed by the Pd/CMI-1, Rh/CMI-1, and Au/CMI-1 catalysts.^[213] Recently, a mesoporous silica SBA-15 with grafted Ti and Fe₂O₃ nanoparticles was reported to exhibit a high yield (up to submmol) and selectivity (≈100%) for partial cyclohexane oxidation with O₂ as the oxidant under solar light (Figure 9B,C).^[214] The high catalytic activity is due to the lengthened lifetime of the tetrahedrally coordinated Ti by electron delocalization in Ti–O–Fe bonds and the visible light-induced activity given by Fe₂O₃ nanoparticles coupled to the Ti. This showcases the capacity of mesoporous silica to work on photocatalytic fine chemical synthesis.

In principle, because MOFs contain a high percentage of transition metals with various possible oxidation states, they appear to be as suitable solid catalysts for oxidations. MOFs have been widely tested as catalysts for epoxidation of cyclohexene in the presence of hydrogen peroxide or TBHP as oxidants. The oxidation of cyclohexene over [Cu(H₂btec)(bipy)]_∞ results in 64.5% conversion and 73.1% selectivity toward cyclohexene oxide at 75 °C in 24 h (Figure 9D).^[215] A 27.5% conversion was achieved over Co^{II}₄O(bdpp)₃ after 22 h using TBHP as the oxidant.^[216] Vanadium containing MOF V-MIL-47 also presents catalytic activity in the cyclohexene oxidation in the liquid phase using TBHP as the oxidant.^[217] Although the pores of V-MIL-47 may be blocked by organic compounds after the first run, its regeneration can be achieved by activating the catalyst at 250 °C for 4 h. In contrast to the current state of using MOFs for oxidation of alkenes, reports of employment of zeolites and mesoporous silica for alkene oxidation are limited. This is because the catalytic transition metals in these porous materials tend to leach out of the framework, rendering them catalytically unstable. The advent of MOFs widened the range of catalysts suitable for selective oxidation reactions with hydrogen peroxide or organic hydroperoxides as oxidants.

MOFs can also be used as supports to include compounds that can function as catalytic sites for the oxidation. For instance, the Pt nanoparticles supported on PCN-224(Zn) show a high yield of >99% toward benzaldehyde in oxidation of benzyl alcohol at 36 °C after 50 min under visible-light irradiation using photochemically generated ¹O₂ as a mild oxidant (Figure 9E,F).^[218] Polyoxotungstates PW₄ and PW₁₂ have been inserted into the nanocages of MIL-101 at a loading range from 5 to 14 wt%, and were tested for cyclohexene oxidation with H₂O₂ as the oxidant.^[219] The results indicate that 5% PW₄/MIL-101 and PW₁₂/MIL-101 both show 76% conversion with 74% selectivity of cyclohexene oxide after 3 h. PW₄/MIL-101 presents a slight decrease in the epoxide yield after three runs, and partial decomposition of the MIL-101 catalyst can be observed during the cyclohexene oxidation. Zr/Hf-based MOFs with high thermal stability and high chemical stability further broaden the catalytic applications of encapsulated nanoparticles.^[58] For example, in oxidation of

cyclopentane (CPE) to glutaraldehyde (GA), UiO-66 encapsulating 35 wt% phosphotungstic acid (HPWs) exhibits a high conversion (≈94.8%) of CPE and a high yield (≈78.3%) of GA with H₂O₂ as the oxidant. The HPWs@UiO-66 catalyst exhibits excellent reusability without obvious HPWs leaching during three reaction cycles, making it a competitively heterogeneous oxidative catalyst.^[220] UiO-66 with highly dispersed Au nanoparticles in the pores, denoted Au@UiO-66, exhibits a high selectivity to benzaldehyde (≈100%) in the oxidation of benzyl alcohol employing O₂ as oxidant. The Au@UiO-66 catalyst also shows good regenerability and high stability during the recycle reactions.^[221,222] Due to its high thermal stability, Au@UiO-66 is also the first example of an MOF-supported Au catalyst for gas-phase CO oxidation. The 4 wt% Au@UiO-66 catalyst exhibits a nearly complete CO conversion at 230 °C and can be reused for at least five reaction cycles.^[102] This work greatly expands the applications of MOFs for gas-phase heterogeneous catalytic reactions.

The organic linkers in MOFs can be modified with chiral functional groups, making MOFs promising materials for asymmetric oxidation catalysis. For example, Hupp and co-workers synthesized a microporous Zn-based MOF containing chiral (salen) Mn complex in its linkers and investigated its catalytic activity for asymmetric epoxidation using 2,2-dimethyl-2H-chromene and 2-(tertbutylsulfonyl) iodosylbenzene as substrate and oxidant, respectively. This MOF exhibits a desirable enantioselective catalytic behavior with a yield of 71%, selectivity of 82%, and prominent recyclability with no selectivity attenuation and very little activity loss. In contrast, the free chiral (salen) Mn complex counterpart shows much poorer catalytic performance in terms of catalytic stability, recyclability, and substrate size selectivity.^[223]

3.4. Hydrogenation

Hydrogenation of unsaturated compounds through the treatment with hydrogen or the reduction in the presence of noble or transition metals (Pt, Ir, Ru, Ni, Pd, etc.) is an important chemical reaction in industry. An easy method for preparing a heterogeneous catalyst containing the above-mentioned reducing metals is successful confinement of these metals into porous zeolite, mesoporous silica, or MOFs. In general, it is desirable for the metals to be in a highly dispersed state to maximize the catalytic activity.

The integration of noble metals with zeolites is a large research field with applications in the chemical and petrochemical industries. Metals have been loaded into zeolites by ion exchange and by impregnation. Pt-Y zeolite, loaded with 14 wt% platinum, showed selective hydrogenation of cinnamaldehyde in the liquid phase (Figure 10A).^[224] The first hydrogenation step leads to 3-phenylpropanal if hydrogenation occurs on the C=C bond or to cinnamyl alcohol if hydrogen adds to the C=O bond. A second hydrogenation step leads to phenylpropanol. Pt and Pd nanoparticles immobilized on the surface of 3-aminopropyltrimethoxysilane (APTS)-functionalized NaY zeolites ([Pt]-APTS-Y and [Pd]-APTS-Y, respectively) are also excellent heterogeneous catalysts for hydrogenation reactions (Figure 10B).^[225] The amine groups in APTS bind strongly to Pt

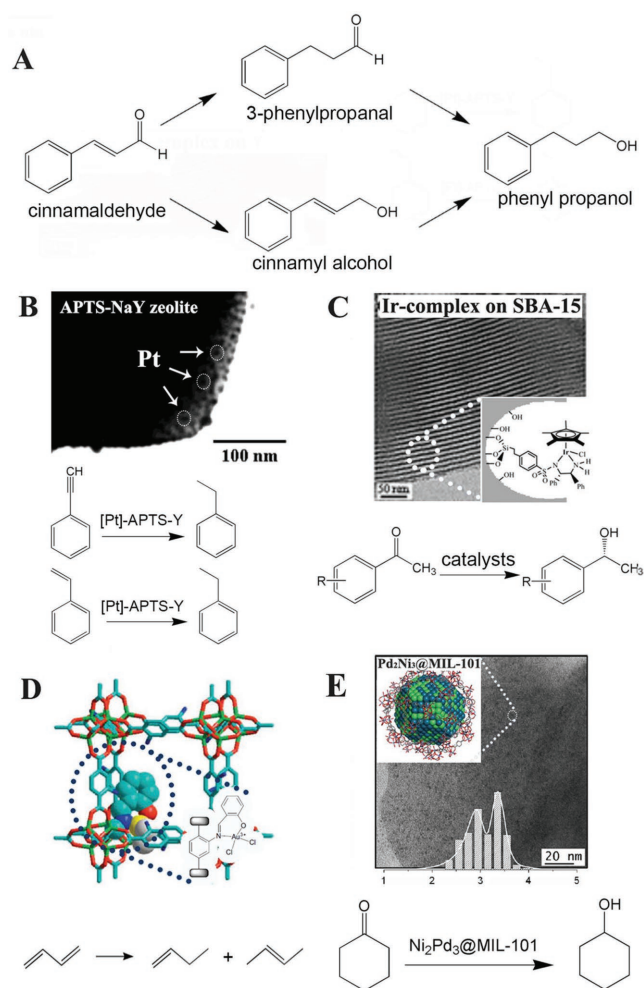


Figure 10. Hydrogenation reaction. A) Hydrogenation of cinnamaldehyde over Pt-Y zeolites. B) TEM image of Pt nanoparticles immobilized on the surface of amine-functionalized Na-Y zeolite. Reproduced with permission.^[225] Copyright 2004, American Chemical Society. C) TEM image of chiral Ir-complex immobilized on mesoporous SBA-15 type materials. Reproduced with permission.^[232] Copyright 2010, Royal Society of Chemistry. D) Schematic of MOFs containing Au(III) Schiff base complex. Zn: green; O: red; C: light blue; N: deep blue; Au: yellow; Cl: white. H atoms are omitted. Reproduced with permission.^[235] Copyright 2009, Elsevier. E) TEM image of Pd₂Ni₃@MIL-101. Reproduced with permission.^[237] Copyright 2012, Wiley-VCH.

and Pd nanoparticles and thus there is no aggregation of metal nanoparticles on the zeolite surface during reactions. In the hydrogenation of styrene, complete conversion with selectivity of 99.2% toward ethylbenzene was achieved by [Pt]-APTS-Y and [Pd]-APTS-Y at 80 °C in 30 min. In hydrogenation of phenylacetylene to ethylbenzene, both catalysts showed a similar conversion of 100%, a selectivity of 66.3% toward ethylbenzene for [Pt]-APTS-Y and a slightly higher selectivity of 85.9% for [Pd]-APTS-Y. Both catalysts can be efficiently recycled three times for hydrogenation reactions.

The hydrogenation function can also be combined with the acidity of zeolites to obtain bifunctional catalysts for use in aromatization, isomerization, polymerization, and hydrocracking reactions. For instance, hydrocracking, which produce

middle-distillate (mainly diesel and lesser extent kerosene) and optionally base oils by a hydrogen addition process, is based on a bifunctional (acidic and metallic) catalyst, such as Pt/USY.^[226,227] The acidic property of Pt/USY determines the activity and selectivity to different fractions (diesel, gases, kerosene, and naphtha) whereas the hydrogenation function is used for hydroconverting sulfur feeds in the second stage hydrocracking unit. So far, no zeolites other than Y have made such significant developments in commercial operations. As in FCC, its extremely high adaptability and well-proven and economical manufacturing process is responsible for its commercial success.

Mesoporous silica with high surface areas also allows for a high dispersion of noble metal ions or transition metal complexes. Pt- and/or Pd-containing Al-MCM-41 was reported as a catalyst for low temperature hydrogenation of benzene and for hydrogenation of aromatics in diesel and kerosene feeds.^[228,229] Pt supported on MCM-41 shows superior catalytic activity in hydrogenation of naphthalene than Pt supported on zeolite USY at 275 °C and 49 atm.^[230] The higher surface area and better Pt dispersion afforded by Pt-MCM-41 should be responsible for the higher hydrogenation activity. For Pt/SBA-15, the selectivity to cinnamyl alcohol is structure sensitive, and large nanoparticles and high hydrogen pressures favor C=O over C=C hydrogenation.^[231] Due to the large pore diameter, mesoporous silica can also serve as a host for metal clusters or transition metal complexes. For example, two chiral Ir and Ru complexes ([Cp*IrCl₂]₂ and [RuCl₂(-C₆Me₆)₂]) were successfully immobilized on mesoporous SBA-15-type materials, leading to two heterogeneous chiral mesoporous catalysts (Figure 10C).^[232] During asymmetric hydrogenation of various aryl substituted ketones under 10 atm H₂, the Ir catalyst exhibited a conversion of up to 92.6% and an *ee* value of 90.3% after 72 h reaction time, whereas the Ru catalyst yielded a conversion of up to 83.4% and an *ee* value of 93.0% after 90 h reaction time. Moreover, both chiral mesoporous catalysts could be easily recovered and used seven times without significantly affecting their catalytic activity and enantioselectivity.

Due to their limited stability, MOFs cannot compete with zeolites and mesoporous silica for hydrogenation reactions in the gas-phase under harsh conditions. Therefore, they are more suitable for liquid-phase catalytic hydrogenation reactions under mild conditions. When 1-octene was treated with a Pd-containing MOF [Pd(2-pymo)₂·3H₂O under mild conditions (30 °C and 1.96 atm H₂), a complete conversion of the substrate was observed after 40 min, and a 100% selectivity toward octane was achieved at a reaction time of 2 h.^[233,234] The Pd-MOF can be reused without structural degradation or leaching of Pd. When an Au(III) MOF was used as a catalyst in hydrogenation of 1,3-butadiene (fixed bed reactor, atmospheric pressure, 130 °C), a near-total conversion and high selectivity (up to 97%) for butenes (mainly 1-butene and E-2-butene) can be obtained (Figure 10D).^[235] MOFs can also act as a host matrix in which the metal nanoparticles, the true catalysts for hydrogenation, are encapsulated. In this context, Pd/MOF-5 embedded with 0.5 wt% Pd was reported to exhibit high catalytic activity for hydrogenation of ethyl cinnamate. Although the Pd/MOF-5 catalyst did not show any loss of activity during repeated runs, a complete loss of micropore volume was observed, indicating

structural collapse. Hence, the active Pd is probably deposited on the outer surface instead of in the micropores of Pd/MOF-5.^[236] Two bimetallic catalysts, Ni₂Pd₃@MIL-101 and Ni₃Pd₂@MIL-101, were found to be catalytically active for hydrogenation of cyclohexanone and 3-heptanone (Figure 10E).^[237] Ni₂Pd₃@MIL-101 shows 100% conversion for cyclohexanone reduction whereas Ni₃Pd₂@MIL-101 results in ≈76% conversion of cycloheptanone. Under analogous conditions, the higher catalytic activity of bimetallic Pd_xNi_y@MIL-101 catalysts for 3-heptanone hydrogenation than a mixture of pure Pd@MIL-101 and Ni-MIL-101 indicates a synergistic catalysis effect due to the formation of bimetallic particles. Recently, Jiang and co-workers observed that the hydrogenation catalysis over MOFs supported nanoparticles can be accelerated under light irradiation. In this regard, a Pd nanocubes@ZIF-8 composite with a core-shell structure efficiently catalyzed the hydrogenation of 1-hexene at a yield of 66% in 30 min under full-spectrum irradiation with 1 atm H₂ at room temperature. Neither activity loss nor apparent aggregation of Pd nanocubes was observed after three continuous runs. The remarkable hydrogenation catalytic performance can be explained by the surface-plasmon-driven photothermal effect induced in Pd nanocubes cores and ZIF-8 shells that leads to hydrogen enrichment and stabilize the Pd nanocubes.^[238] Moreover, MOFs supported transition metal complexes can further broaden their applications in asymmetric hydrogenation catalysis. For instance, a Ru-complex incorporated Zr-MOF can catalyze hydrogenation of a broad range of substituted alkenes with *ee* values of 70%–91% and hydrogenation of β-keto esters into corresponding alcohols with high selectivity (*ee* > 94%) in a quantitative yield.^[239]

4. Conclusions and Future Prospects

Heterogeneous catalysis is an explored application of zeolites, mesoporous silica, and MOFs. A wide range of organic reactions has been catalyzed with these porous materials, from acid-base to redox categories. In this review, we provided several typical examples of zeolites, mesoporous silica, and MOFs as catalysts in gas/liquid-phase reactions and compared their catalytic performance and potential for the same reactions. From these examples, the following can be summarized.

Zeolites still dominate gas-phase reactions. Many well-established processes in oil refining and petrochemistry, including aromatic alkylation, FCC, oligomerization of light olefins, and hydrocracking use zeolite-based catalysts. The success of zeolites in this field relies on their microporous structures in the range of molecular dimensions and flexible chemical composition, and on their outstanding thermal and hydrothermal stability. In addition, deactivated zeolites can be easily reactivated by combustion to remove coke or heavier residual products. In this regard, it is difficult for MOFs and mesoporous silica to compete with zeolites for this type of application. The use of MOFs for gas-phase catalysis is in an early phase and most investigations are focused on proof-of-concept reactions. Mesoporous silica may have great potential for use in FCC catalysis, as deduced from the importance of mesopores for zeolite Y to crack bulky molecules in the FCC process.

Mesoporous silica and MOFs can complement zeolites in the synthesis of fine chemicals that proceeds under relatively mild conditions in a liquid phase, i.e., Friedel-Crafts acylation, cycloaddition of CO₂ into epoxides, ring opening of epoxides, Knoevenagel condensation, and alkene oxidation. These reactions can be roughly divided according to decisive characteristics providing catalytic activity. The first group of reactions primarily depends on the nature of active centers (e.g., Friedel-Crafts acylation, ring opening of epoxides, and cycloaddition of CO₂ into epoxides). In this case, zeolites with adventitious acid sites tend to open the epoxide ring very easily, mesoporous silica demonstrates a good potential for the Friedel-Crafts acylation of organic molecules that require lower level of acidity, and MOFs that have both acid and base sites are suited for cycloaddition of CO₂ into epoxides. The second group of reactions is influenced by interactions between substrates, intermediates, or products with active sites (e.g., Knoevenagel condensation). The specific interactions have positive impacts on the catalytic behavior of MOFs, compared with negligible influence of interactions on zeolites. The last group of reactions is sensitive to the size of the channels in the catalysts (e.g., alkene oxidation). In this case, mesoporous silica with larger pores than those of zeolites exhibits better catalytic performance in oxidation of bulky alkenes. In contrast, zeolites are more active in oxidation of small substrates that have no obvious diffusion issue for medium pores.

Although zeolites have been widely used as catalysts in the fields of refining and petrochemistry, catalyst improvement for higher selectivity or longer catalyst lifetime is still needed. In addition, the application of zeolites in base-catalyzed processes has faced challenges from inexpensive NaOH and KOH. Thus, the synthesis of known zeolites using alternative and less expensive routes is necessary. As crude oils have a tendency of being heavier, new zeolites with larger pore size and lower cost are also desirable. For production of chemicals and fine chemicals, the leaching of metals from the zeolite framework is a particular problem, especially in oxidation reactions. Therefore, it is necessary to discover the stability of zeolites and leaching of active metal species by comparing the crystal structure and surface area before and after the reactions.

For mesoporous silica and MOFs, a major drawback for their use as catalysts is their relatively limited thermal and chemical stability. In the last few years, a large step forward has been made on this road. However, on the other hand, asymmetric catalysis appears as a promising area in which mesoporous silica and MOFs can easily make significant contributions. Chiral mesoporous silica can be obtained by fixing region- and enantioselective complexes in the large pores. In addition to immobilization, chiral MOFs can be easily synthesized by employing chiral and enantiopure organic molecules as the linkers. In this case, the stability is not a major problem for the two porous materials because of the mild reaction conditions. Because all the three components (nodes, linkers, and pores) in MOFs can be functionally modified, MOFs further find interesting applications in photochemistry, synergistic catalysis, and tandem reaction. Numbers of reviews have summarized the use of MOFs in these reactions.^[56–59] Thus, in addition to gas phase catalysis, there are broad catalytic areas where mesoporous silica and MOFs can exploit their advantages to the full.

All in all, zeolite, mesoporous silica and MOFs provide excellent potential for development of heterogeneous catalytic systems. The similarities and differences in the use of zeolites, mesoporous silica and MOFs as heterogeneous catalysts make them complementary rather than competitive. These porous materials can be used for different reactions or for the same reaction under different conditions. We should make use of the most adequate catalyst for a particular reaction regardless if it is a zeolite, mesoporous silica, or an MOF.

Acknowledgements

J.L. and Z.L. contributed equally to this work. This work was financially supported by the Singapore Academic Research Fund (RG112/15 and RG19/16), the National Natural Science Foundation of China (No. 21371014), and the National Program for Support of Top-notch Young Professionals.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

heterogeneous catalysis, mesoporous silica, metal–organic frameworks, porous materials, zeolites

Received: February 27, 2017

Revised: April 2, 2017

Published online:

- [1] J. B. Nagy, P. Bodart, I. Hannus, I. Kiricsi, *Synthesis, Characterization and Use of Zeolitic Microporous Materials*, Decagen Ltd., Szeged, Hungary **1998**.
- [2] J. Čejka, A. Corma, S. Zones, *Zeolites and Catalysis: Synthesis, Reactions and Applications*, Vol. 2, Wiley-VCH, Weinheim, Germany **2010**.
- [3] J. Čejka, B. Wichterlová, S. Bednářová, *Appl. Catal.* **1991**, 79, 215.
- [4] G. Centi, S. Perathoner, in *Zeolites and Catalysis: Synthesis, Reactions and Applications*, Vol. 2 (Eds: J. Čejka, A. Corma, S. I. Zones), Wiley-VCH, Weinheim, Germany **2010**, p. 745.
- [5] G. Centi, B. Wichterlová, A. T. Bell, *Catalysis by Unique Metal Ion Structures in Solid Matrices: From Science to Application*, NATO Science Series II, Springer, The Netherlands **2001**.
- [6] J. Čejka, J. Pérez-Pariente, W. J. Roth, *Zeolites: From Model Materials to Industrial Catalysts*, Transworld Research Network, Singapore **2008**.
- [7] Database of Zeolite Structures, <http://www.iza-structure.org/databases/> (accessed: March, 2017).
- [8] A. Corma, M. E. Davis, *ChemPhysChem* **2004**, 5, 304.
- [9] a) M. Moliner, C. Martínez, A. Corma, *Angew. Chem., Int. Ed.* **2015**, 54, 3560; b) *Angew. Chem.* **2015**, 127, 5750.
- [10] J. L. Sun, C. Bonneau, Á. Cantin, A. Corma, M. J. Diaz-Cabañas, M. Moliner, D. L. Zhang, M. R. Li, X. D. Zou, *Nature* **2009**, 458, 1154.
- [11] R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic, London **1978**.
- [12] D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, John Wiley and Sons, New York **1974**.
- [13] S. Zones, presented at the 16th Int. Zeolite Conf. Sorrento, Italy, July **2010**.
- [14] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. S. Beck, *Nature* **1992**, 359, 710.
- [15] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, K. D. Schmidt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, 114, 10834.
- [16] K. Schumacher, P. I. Ravikovitch, A. D. Chesne, A. V. Neimark, K. K. Unger, *Langmuir* **2000**, 16, 4648.
- [17] Q. Huo, R. Leon, P. M. Petroff, G. D. Stucky, *Science* **1995**, 268, 1324.
- [18] Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, 8, 1147.
- [19] S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, K. Kuroda, *Bull. Chem. Soc. Jpn.* **1996**, 69, 1449.
- [20] D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, 279, 548.
- [21] A. S. Poyraz, C. H. Kuo, S. Biswas, C. K. King'ondo, S. L. Suib, *Nat. Commun.* **2013**, 4, 10.
- [22] P. Tan, J.-X. Qin, X.-Q. Liu, X.-Q. Yin, L.-B. Sun, *J. Mater. Chem. A* **2014**, 2, 4698.
- [23] M. Yang, S. Li, Y. Wang, J. A. Herron, Y. Xu, L. F. Allard, S. Lee, J. Huang, M. Mavrikakis, M. Flytzani-Stephanopoulos, *Science* **2014**, 346, 1498.
- [24] L. B. Sun, *Curr. Org. Chem.* **2014**, 18, 1225.
- [25] J. Kou, C. Bennett-Stamper, R. S. Varma, *Nanoscale* **2011**, 3, 4958.
- [26] Y. Yin, D.-M. Xue, X.-Q. Liu, G. Xu, P. Ye, M.-Y. Wu, L.-B. Sun, *Chem. Commun.* **2012**, 48, 9495.
- [27] W. Li, J. Liu, D. Zhao, *Nat. Rev. Mater.* **2016**, 1, 16023.
- [28] P. Prokešová, N. Žilková, S. Mintova, T. Bein, J. Čejka, *Appl. Catal. A* **2005**, 281, 85.
- [29] J. Perez-Ramirez, C. H. Christensen, K. Egeblad, C. H. Christensen, J. C. Groen, *Chem. Soc. Rev.* **2008**, 37, 2530.
- [30] J. Perez-Ramirez, D. Verboekend, A. Bonilla, S. Abello, *Adv. Funct. Mater.* **2009**, 19, 3972.
- [31] Z. Musilová-Pavlačková, S. I. Zones, J. Čejka, *Top. Catal.* **2010**, 53, 273.
- [32] M. S. Holm, E. Taarning, K. Egeblad, C. H. Christensen, *Catal. Today* **2011**, 168, 3.
- [33] V. Valtchev, S. Mintova, M. Tsapatsis, *Ordered Porous Solids*, Elsevier Science, Amsterdam, Netherlands **2009**.
- [34] S. Wang, T. Dou, Y. Li, Y. Zhang, X. Li, Z. Yan, *Catal. Commun.* **2005**, 6, 87.
- [35] S. Inagaki, M. Ogura, T. Inami, Y. Sasaki, E. Kikuchi, M. Matsukata, *Microporous Mesoporous Mater.* **2004**, 74, 163.
- [36] J. Y. Ying, J. Garcia-Martinez (Massachusetts Institute of Technology), *US7589041* **2009**.
- [37] a) A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem., Int. Ed.* **1999**, 38, 3268; b) *Angew. Chem.* **1999**, 111, 3466.
- [38] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Chem. Commun.* **2012**, 48, 11275.
- [39] A. Corma, H. Garcia, F. Xamena, *Chem. Rev.* **2010**, 110, 4606.
- [40] M. Wang, M. H. Xie, C. D. Wu, Y. G. Wang, *Chem. Commun.* **2009**, 2396.
- [41] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, 423, 705.
- [42] a) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* **2004**, 43, 2334; b) *Angew. Chem.* **2004**, 116, 2388.
- [43] a) D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem., Int. Ed.* **2009**, 48, 7502; b) *Angew. Chem.* **2009**, 121, 7638.
- [44] M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, 34, 319.
- [45] S. T. Meek, J. A. Greathouse, M. D. Allendorf, *Adv. Mater.* **2011**, 23, 249.
- [46] O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, s. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. O. Yazaydin, J. T. Hupp, *J. Am. Chem. Soc.* **2012**, 134, 15016.

- [47] H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, *Science* **2012**, 336, 1018.
- [48] A. Corma, H. García, F. X. Llabrés i Xamena, *Chem. Rev.* **2010**, 110, 4606.
- [49] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* **2014**, 43, 6011.
- [50] A. Dhakshinamoorthy, M. Alvaro, A. Corma, H. Garcia, *Dalton Trans.* **2011**, 40, 6344.
- [51] A. Dhakshinamoorthy, M. Opanaseno, J. Čejka, H. Garcia, *Catal. Sci. Technol.* **2013**, 3, 2509.
- [52] J. Gascon, A. Corma, F. Kapteijn, F. X. Llabrés i Xamena, *ACS Catal.* **2014**, 4, 361.
- [53] M. Ranocchiaro, J. A. v. Bokhoven, *Phys. Chem. Chem. Phys.* **2011**, 13, 6388.
- [54] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* **2014**, 43, 6011.
- [55] A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, F. Verpoort, *Chem. Soc. Rev.* **2015**, 44, 6804.
- [56] L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, 38, 1248.
- [57] H. He, J. A. Perman, G. Zhu, S. Ma, *Small* **2016**, 12, 6309.
- [58] M. Rimoldi, A. J. Howarth, M. R. DeStefano, L. Lin, S. Goswami, P. Li, J. T. Hupp, O. K. Farha, *ACS Catal.* **2017**, 7, 997.
- [59] Y.-B. Huang, J. Liang, X.-S. Wang, R. Cao, *Chem. Soc. Rev.* **2017**, 46, 126.
- [60] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, 309, 2040.
- [61] J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.* **2008**, 130, 13850.
- [62] S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.* **2007**, 129, 14176.
- [63] T. C. Wang, N. A. Vermeulen, I. S. Kim, A. B. F. Martinson, J. F. Stoddart, J. T. Hupp, O. K. Farha, *Nat. Protoc.* **2016**, 11, 149.
- [64] D. Feng, H.-L. Jiang, Y.-P. Chen, Z.-Y. Gu, Z. Wei, H.-C. Zhou, *Inorg. Chem.* **2013**, 52, 12661.
- [65] a) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, *Angew. Chem., Int. Ed.* **2012**, 51, 10307; b) *Angew. Chem.* **2012**, 124, 10343.
- [66] D. Feng, Z.-Y. Gu, Y.-P. Chen, J. Park, Z. Wei, Y. Sun, M. Bosch, S. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.* **2014**, 136, 17714.
- [67] D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg, H.-C. Zhou, *J. Am. Chem. Soc.* **2013**, 135, 17105.
- [68] P. Kumar, K. V. Agrawal, M. Tsapatsis, K. A. Mkhoyan, *Nat. Commun.* **2015**, 6, 7128.
- [69] X. Guo, Y. Feng, L. Ma, D. Gao, J. Jing, J. Yu, H. Sun, H. Gong, Y. Zhang, *Appl. Surf. Sci.* **2017**, 402, 53.
- [70] a) C. Avci, J. Ariñez-Soriano, A. Carné-Sánchez, V. Guillerm, C. Carbonell, I. Imaz, D. Maspoch, *Angew. Chem., Int. Ed.* **2015**, 54, 14417; b) *Angew. Chem.* **2015**, 127, 14625.
- [71] M. Ranocchiaro, C. Lothschätz, D. Grolimund, J. A. van Bokhoven, *Proc. R. Soc. A* **2012**, 468, 1985.
- [72] S. Samanta, N. K. Mal, A. Bhaumik, *J. Mol. Catal. A: Chem.* **2005**, 236, 7.
- [73] N. Pal, E.-B. Cho, D. Kim, *RSC Adv.* **2014**, 4, 9213.
- [74] A. Bhaumik, T. Tatsumi, *J. Catal.* **2000**, 189, 31.
- [75] Y. Zhang, F. Gao, H. Wan, C. Wu, Y. Kong, X. Wu, B. Zhao, L. Dong, Y. Chen, *Microporous Mesoporous Mater.* **2008**, 113, 393.
- [76] W. Huang, J. N. Kuhn, C.-K. Tsung, Y. Zhang, S. E. Habas, P. Yang, G. A. Somorjai, *Nano Lett.* **2008**, 8, 2027.
- [77] A. Dhakshinamoorthy, H. Garcia, *Chem. Soc. Rev.* **2012**, 41, 5262.
- [78] J. Juan-Alcañiz, J. Gascon, F. Kapteijn, *J. Mater. Chem.* **2012**, 22, 10102.
- [79] P. Falcaro, R. Ricco, A. Yazdi, I. Imaz, S. Furukawa, D. Maspoch, R. Ameloot, J. D. Evans, C. J. Doonan, *Coord. Chem. Rev.* **2016**, 307, 237.
- [80] P. García-García, M. Müller, A. Corma, *Chem. Sci.* **2014**, 5, 2979.
- [81] G. Cruciani, *J. Phys. Chem. Solids* **2006**, 67, 1973.
- [82] X. S. Zhao, F. Audsley, G. Q. Lu, *J. Phys. Chem. B* **1998**, 102, 4143.
- [83] S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.* **2007**, 129, 14176.
- [84] J. J. Low, A. I. Benin, P. Jakubczak, J. F. Abrahamian, S. A. Faheem, R. R. Willis, *J. Am. Chem. Soc.* **2009**, 131, 15834.
- [85] a) M. Zhang, Y. P. Chen, M. Bosch, T. Gentle, K. Wang, D. Feng, Z. U. Wang, H. C. Zhou, *Angew. Chem., Int. Ed.* **2014**, 53, 815; b) *Angew. Chem.* **2014**, 126, 834.
- [86] L. Valenzano, B. Civalieri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud, C. Lamberti, *Chem. Mater.* **2011**, 23, 1700.
- [87] H. van Bekkum, E. M. Flanigen, J. C. Jansen, in *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam, The Netherlands **1991**.
- [88] A. Corma, *Chem. Rev.* **1997**, 97, 2373.
- [89] F. Di Renzo, F. Fajula, in *Zeolites and Ordered Mesoporous Materials: Progress and Prospects*, Vol. 157 (Eds: J. Čejka, H. van Bekkum), Elsevier, Amsterdam, The Netherlands **2005**, p. 1.
- [90] M. J. Climent, A. Corma, S. Iborra, *Chem. Rev.* **2011**, 111, 1072.
- [91] A. Corma, S. Iborra, S. Miquel, J. Primo, *J. Catal.* **1998**, 173, 315.
- [92] R. A. Sheldon, R. S. Downing, *Appl. Catal. A* **1999**, 189, 163.
- [93] J. H. Clark, *Acc. Chem. Res.* **2002**, 35, 791.
- [94] R. A. Sheldon, *Green Chem.* **2007**, 9, 1273.
- [95] L. Ackermann, *Chem. Rev.* **2011**, 111, 1315.
- [96] F. Collet, C. Lescot, P. Dauban, *Chem. Soc. Rev.* **2011**, 40, 1926.
- [97] a) G. W. Coates, D. R. Moore, *Angew. Chem., Int. Ed.* **2004**, 43, 6618; b) *Angew. Chem.* **2004**, 116, 6784.
- [98] N. Pal, A. Bhaumik, *RSC Adv.* **2015**, 5, 24363.
- [99] A. Dhakshinamoorthy, M. Opanasenko, J. Čejka, H. Garcia, *Catal. Sci. Technol.* **2013**, 3, 2509.
- [100] H. G. T. Nguyen, N. M. Schweitzer, C.-Y. Chang, T. L. Drake, M. C. So, P. C. Stair, O. K. Farha, J. T. Hupp, S. T. Nguyen, *ACS Catal.* **2014**, 4, 2496.
- [101] S. Lee, M. D. Vece, B. Lee, S. Seifert, R. E. Winans, S. Vajda, *Phys. Chem. Chem. Phys.* **2012**, 14, 9336.
- [102] R. Wu, X. Qian, K. Zhou, H. Liu, B. Yadian, J. Wei, H. Zhu, Y. Huang, *J. Mater. Chem. A* **2013**, 1, 14294.
- [103] M. V. Baldoší, A. Corma, V. Fornés, H. García, A. Martínez, J. Primo, *J. Chem. Soc. Chem. Commun.* **1992**, 949.
- [104] A. Corma, H. Garcia, A. Primo, A. Domenech, *New J. Chem.* **2004**, 28, 361.
- [105] K. Tanabe, W. F. Hölderich, *Appl. Catal., A* **1999**, 181, 399.
- [106] T. F. Degnan, C. M. Smith, C. R. Venkat, *Appl. Catal., A* **2001**, 221, 283.
- [107] 2005 Petrochemical Processes, *Hydrocarbon Processing*, Gulf Publishing Company, Houston, TX, USA **2005**.
- [108] R. F. Guarino, C. H. Li, *Hydrocarbon Eng.* **1999**, 4, 39.
- [109] R. J. Schmidt, in *Encyclopedia of Chemical Processing, Cumene* (Ed: S. Lee), Taylor & Francis, New York **2006**, p. 603.
- [110] T. F. Degnan, C. M. Smith, C. R. Venkat, *Appl. Catal. A* **2001**, 221, 283.
- [111] C. Perego, P. Ingallina, *Catal. Today* **2002**, 73, 3.
- [112] Q. N. Le (Mobile Oil Corp.), *US5118894* **1992**.
- [113] G. Bellussi, C. Perego, A. Carati, S. Peratello, E. Previde Massara, G. Pergo, *Stud. Surf. Sci. Catal.* **1994**, 84, 85.
- [114] A. Corma, B. W. Wojciechowski, *Catal. Rev. Sci. Eng.* **1985**, 27, 29.
- [115] C. Perego, A. Carati, in *Zeolites: from Model Materials to Industrial Catalysts* (Eds: J. Čejka, J. Pérez-Pariente, W. J. Roth), Transworld Research Network, Singapore **2008**, p. 357.
- [116] A. Corma, A. Martínez, in *Zeolites and Ordered Mesoporous Materials: Progress and Prospects*, Vol. 157 (Eds: J. Čejka, H. van Bekkum), Elsevier, Amsterdam, The Netherlands **2005**, p. 337.

- [117] M. Rigutto, in *Zeolites and Catalysis, Synthesis, Reactions and Applications*, Vol. 2 (Eds: J. Čejka, A. Corma, S. Zones), Wiley-VCH, Weinheim, Germany **2010**, p. 547.
- [118] A. A. Avidan, *Stud. Surf. Sci. Catal.* **1993**, 76, 1.
- [119] a) K. P. de Jong, J. Zečević, H. Friedrich, P. E. de Jongh, M. Bulut, S. van Donk, R. Kenmogne, A. Finiels, V. Hulea, F. Fajula, *Angew. Chem., Int. Ed.* **2010**, 49, 10074; b) *Angew. Chem.* **2010**, 122, 10272.
- [120] J. Dwyer, D. Millward, P. J. O'Malley, A. Araya, A. Corma, V. Fornes, A. Martinez, *J. Chem. Soc., Faraday Trans.* **1990**, 86, 1001.
- [121] A. Haas, *Microporous Mesoporous Mater.* **1999**, 28, 325.
- [122] A. Corma, M. J. Díaz-Cabañas, F. Rey, J. Rius, *Nature* **2002**, 418, 514.
- [123] A. Corma Canos, M. J. Díaz-Cabañas, J. Martínez-Triguero, F. Rey-García, *EP1445297* **2004**.
- [124] M. Moliner, M. J. Díaz-Cabañas, V. Fornes, C. Martinez, A. Corma, *J. Catal.* **2008**, 254, 101.
- [125] A. Corma, M. S. Grande, V. Gonzales-Alfaro, A. V. Orchilles, *J. Catal.* **1996**, 159, 375.
- [126] H. Koch, W. Reschetilowski, *Microporous Mesoporous Mater.* **1998**, 25, 127.
- [127] J.-W. Da, C.-M. Song, L. Qian, J.-M. Su, X.-Z. Xu, *J. Porous Mater.* **2008**, 15, 189.
- [128] H. Owen, S. K. Marsh, B. S. Wright, *US4456779* **1984**.
- [129] S. Tabak, *US4433185* **1984**.
- [130] P. M. M. Blauwhoff, J. W. Gosselink, E. P. Kieffer, S. T. Sie, W. H. J. Stork, in *Catalysis and Zeolites: Fundamentals and Applications* (Eds: J. Weitkamp, L. Puppe), Springer-Verlag, Berlin, Germany **1999**, p. 437.
- [131] L. M. Kustov, V. Y. Borovkov, V. B. Kazanskii, *Stud. Surf. Sci. Catal.* **1984**, 18, 241.
- [132] C. S. H. Chen, R. F. Bridger, *J. Catal.* **1996**, 161, 687.
- [133] N. M. Page, L. B. Young, D. A. Blain, *US4870038* **1989**.
- [134] K. G. Wilshier, P. Smart, R. Western, T. Mole, T. Behrsing, *Appl. Catal.* **1987**, 31, 339.
- [135] L. R. Martens, J. P. Verduijn, G. M. Mathys, *Catal. Today* **1997**, 36, 451.
- [136] S. W. Beadle, *WO 2003082779* **2003**.
- [137] C. B. Duncan, *WO2003082781* **2003**.
- [138] M. R. Apelian, J. R. Boulton, A. S. Fung, *US5284989* **1994**.
- [139] R. J. Quann, L. A. Green, S. A. Tabak, F. J. Krambeck, *Ind. Eng. Chem. Res.* **1988**, 27, 565.
- [140] G. Bellusi, F. Cavani, V. Arrigoni, R. Ghezzi, *EP0463673* **1992**.
- [141] B. Chiche, E. Sauvage, F. Di Renzo, I. I. Ivanova, F. Fajula, *J. Mol. Catal. A* **1998**, 134, 145.
- [142] X. Zhang, F. X. Llabrés i Xamena, A. Corma, *J. Catal.* **2009**, 265, 155.
- [143] G. Sartori, R. Maggi, *Chem. Rev.* **2006**, 106, 1077.
- [144] B. I. Roman, N. De Kimpe, C. V. Stevens, *Chem. Rev.* **2010**, 110, 5914.
- [145] M. Bejblova, D. Prochazkova, J. Čejka, *ChemSusChem* **2009**, 2, 486.
- [146] S. G. Waghholkar, P. S. Niphadkar, S. Mayadevi, S. Sivasanker, *Appl. Catal., A* **2007**, 317, 250.
- [147] C. Guignard, V. Pedron, F. Richard, R. Jacquot, M. Spagnol, J. M. Coustard, G. Perot, *Appl. Catal. A* **2002**, 234, 79.
- [148] M. Casagrande, L. Storaro, M. Lenarda, R. Ganzerla, *Appl. Catal. A* **2000**, 201, 263.
- [149] D. Procházková, M. Bejblová, J. Vlk, A. Vinu, P. Štěpnička, J. Čejka, *Chem. Eur. J.* **2010**, 16, 7773.
- [150] L. Červený, K. Mikulcová, J. Čejka, *Appl. Catal., A* **2002**, 223, 65.
- [151] A. Corma, *Chem. Rev.* **1995**, 95, 559.
- [152] C. Guignard, V. Pedron, F. Richard, R. Jacquot, M. Spagnol, J. M. Coustard, G. Perot, *Appl. Catal., A* **2002**, 234, 79.
- [153] L. Kurfiřtová, Y.-K. Seo, Y. K. Hwang, J.-S. Chang, J. Čejka, *Catal. Today* **2012**, 179, 85.
- [154] Z. El Berrichi, L. Cherif, J. P. Tessonnier, B. Louis, J. Fraissard, M. J. Ledoux, C. Pham-Huu, *Stud. Surf. Sci. Catal.* **2005**, 158, 1413.
- [155] F. Z. El Berrichi, C. Pham-Huu, L. Cherif, B. Louis, M. J. Ledoux, *Catal. Commun.* **2011**, 12, 790.
- [156] Y. Zhou, S. Hu, X. Ma, S. Liang, T. Jiang, B. Han, *J. Mol. Catal. A: Chem.* **2008**, 284, 52.
- [157] J. N. Appaturi, F. Adam, *Appl. Catal., B* **2013**, 136, 150.
- [158] X. B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, 41, 1462.
- [159] T. Chang, H. Jing, L. Jin, W. Qiu, *J. Mol. Catal. A: Chem.* **2007**, 264, 241.
- [160] R. L. Paddock, Y. Hiyama, J. M. McKay, S. T. Nguyen, *Tetrahedron Lett.* **2004**, 45, 2023.
- [161] X. Lu, H. Wang, R. He, *J. Mol. Catal. A: Chem.* **2002**, 186, 33.
- [162] R. L. Paddock, S. T. Nguyen, *J. Am. Chem. Soc.* **2001**, 123, 11498.
- [163] E. J. Doskocil, S. V. Bordawekar, B. G. Kaye, R. J. Davis, *J. Phys. Chem. B* **1999**, 103, 6277.
- [164] C.-G. Li, L. Xu, P. Wu, H. Wu, M. He, *Chem. Commun.* **2014**, 50, 15764.
- [165] C. M. Miralda, E. E. Macias, M. Q. Zhu, P. Ratnasamy, M. A. Carreon, *ACS Catal.* **2012**, 2, 180.
- [166] P.-Z. Li, X.-J. Wang, J. Liu, J. S. Lim, R. Zou, Y. Zhao, *J. Am. Chem. Soc.* **2016**, 138, 2142.
- [167] J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang, B. Han, *Green Chem.* **2009**, 3552.
- [168] O. V. Zalomaeva, A. M. Chibiryayev, K. A. Kovalenko, O. A. Kholdeeva, B. S. Balzhinimaev, V. P. Fedin, *J. Catal.* **2013**, 298, 179.
- [169] O. V. Zalomaeva, N. V. Maksimchuk, A. M. Chibiryayev, K. A. Kovalenko, V. P. Fedin, B. S. Balzhinimaev, *J. Energy Chem.* **2013**, 22, 130.
- [170] R. Srivastava, D. Srinivas, P. Ratnasamy, *J. Catal.* **2005**, 233, 1.
- [171] J. S. Yadav, A. Reddy, N. A. V. Ramesh, B. V. S. Reddy, *J. Mol. Catal. A: Chem.* **2007**, 261, 207.
- [172] R. I. Kureshy, S. Singh, N. H. Khan, S. H. R. Abdi, E. Suresh, R. V. Jasra, *J. Mol. Catal. A Chem.* **2007**, 264, 162.
- [173] R. I. Kureshy, S. Agrawal, M. Kumar, N. H. Khan, S. H. R. Abdi, H. C. Bajaj, *Catal. Lett.* **2010**, 134, 318.
- [174] B. Tang, W. Dai, G. Wu, N. Guan, L. Li, M. Hunger, *ACS Catal.* **2014**, 4, 2801.
- [175] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Chem. Eur. J.* **2010**, 16, 8530.
- [176] S. M. F. Vilela, D. Ananias, J. A. Fernandes, P. Silva, A. C. Gomes, N. J. O. Silva, M. O. Rodrigues, J. P. C. Tomé, A. A. Valente, P. Ribeiro-Claro, L. D. Carlos, J. Rocha, F. A. A. Paz, *J. Mater. Chem. C* **2014**, 2, 3311.
- [177] Y.-X. Zhou, Y.-Z. Chen, Y. Hu, G. Huang, S.-H. Yu, H.-L. Jiang, *Chem. Eur. J.* **2014**, 20, 14976.
- [178] K. Tanaka, S. Oda, M. Shiro, *Chem. Commun.* **2008**, 44, 820.
- [179] S. Budhi, C. Peeraphatdit, S. Pylypenkoc, Vy H. T. Nguyen, E. A. Smith, B. G. Trewyn, *Appl. Catal., A* **2014**, 475, 469.
- [180] M. W. C. Robinson, R. Buckle, I. Mabbett, G. M. Grant, A. E. Graham, *Tetrahedron Lett.* **2007**, 48, 4723.
- [181] A. Bordoloi, Y. K. Hwang, J.-S. Hwang, S. B. Halligudi, *Catal. Commun.* **2009**, 10, 1398.
- [182] P. Dutta, P. Kalita, P. K. Baruah, *ChemistrySelect* **2016**, 1, 1650.
- [183] P. Srinivasu, S. Alam, V. V. Balasubramanian, S. Velmathi, D. P. Sawant, W. Bohlmann, S. P. Mirajkar, K. Ariga, S. B. Halligudi, A. Vinu, *Adv. Funct. Mater.* **2008**, 18, 640.
- [184] C. J. Gommers, H. Friedrich, M. Wolters, P. E. de Jongh, K. P. de Jong, *Chem. Mater.* **2009**, 21, 1311.
- [185] A. Zukal, H. Sjiklova, J. Čejka, *Langmuir* **2008**, 24, 9837.
- [186] A. Corma, V. Fornés, R. M. Martín-Aranda, H. García, J. Primo, *Appl. Catal.* **1990**, 59, 237.
- [187] A. Corma, R. M. Martín-Aranda, F. Sanchez, *J. Catal.* **1990**, 126, 192.

- [188] S. Saravanamurugan, M. Palanichamy, M. Hartmann, V. Murugesan, *Appl. Catal. A* **2006**, 298, 8.
- [189] X. Wang, K. S. K. Lin, J. C. C. Chan, S. Cheng, *J. Phys. Chem. B* **2005**, 109, 1763.
- [190] F. P. Shang, J. R. Sun, S. J. Wu, Y. Yang, Q. B. Kan, J. Q. Guan, *Microporous Mesoporous Mater.* **2010**, 134, 44.
- [191] H. Zhao, N. Yu, Y. Ding, R. Tan, C. Liu, D. Yin, H. Qiu, D. Yin, *Microporous Mesoporous Mater.* **2010**, 136, 10.
- [192] T. Wang, G. Wu, N. Guan, L. Li, *Microporous Mesoporous Mater.* **2012**, 148, 184.
- [193] a) Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Ferey, *Angew. Chem., Int. Ed.* **2008**, 47, 4144; b) *Angew. Chem.* **2008**, 120, 4212.
- [194] J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink, F. Kapteijn, *J. Catal.* **2009**, 261, 75.
- [195] J. Park, J. R. Li, Y. P. Chen, J. M. Yu, A. A. Yakovenko, Z. Y. U. Wang, L. B. Sun, P. B. Balbuena, H. C. Zhou, *Chem. Commun.* **2012**, 48, 9995.
- [196] C. Perego, A. Carati, P. Ingallina, M. A. Mantegazza, G. Bellussi, *Appl. Catal. A* **2001**, 221, 63.
- [197] P. Roffia, G. Leofanti, A. Cesana, M. Mantegazza, M. Padovan, G. Petrini, S. Tonti, P. Gervasutti, *Chim. Ind.* **1990**, 72, 598.
- [198] S. Tonti, P. Roffia, V. Gervasutti, *US5227525* **1993**.
- [199] P. Roffia, G. Leofanti, A. Cesana, M. Mantegazza, M. Padovan, G. Petrini, S. Tonti, P. Gervasutti, *Stud. Surf. Sci. Catal.* **1990**, 55, 43.
- [200] A. Thangaraj, S. Sivasanker, P. Ratnasamy, *J. Catal.* **1991**, 131, 394.
- [201] H. Xu, Y. T. Zhang, H. H. Wu, Y. M. Liu, X. H. Li, J. G. Jiang, M. Y. He, W. Peng, *J. Catal.* **2011**, 281, 263.
- [202] B. J. Le, J. Dakka, R. A. Sheldon, *Appl. Catal. A* **1996**, 136, 69.
- [203] J. S. Reddy, S. Sivasanker, P. Ratnasamy, *J. Mol. Catal.* **1991**, 69, 383.
- [204] P. Wu, P. Komatsu, T. Yashima, *J. Catal.* **1997**, 168, 400.
- [205] F. Song, Y. M. Liu, H. H. Wu, M. Y. He, P. Wu, T. Tatsumi, *J. Catal.* **2006**, 237, 359.
- [206] F. Song, Y. M. Liu, L. L. Wang, H. J. Zhang, M. Y. He, P. Wu, *Appl. Catal. A* **2007**, 327, 22.
- [207] S. Zhao, W. Xie, J. X. Yang, Y. M. Liu, Y. T. Zhang, B. L. Xu, J.-G. Jiang, M. Y. He, P. Wu, *Appl. Catal. A* **2011**, 394, 1.
- [208] T. Blasco, A. Corma, M. T. Navarro, J. Pérez Pariente, *J. Catal.* **1995**, 156, 65.
- [209] F. Xiao, Y. Han, Y. Yu, X. Meng, M. Yang, S. Wu, *J. Am. Chem. Soc.* **2002**, 124, 888.
- [210] A. Corma, M. E. Domine, J. A. Gaona, J. L. Jorda, M. T. Navarro, F. Rey, J. Perez-Pariente, J. Tsuji, B. McCulloch, L. T. Nemeth, *Chem. Commun.* **1998**, 2211.
- [211] B. S. Uphade, Y. Yamada, T. Akita, T. Nakamura, M. Haruta, *Appl. Catal. A* **2001**, 215, 137.
- [212] R. Li, X. Yan, X. Zhu, D. Shou, X. Zhou, Y. Dai, Y. Yang, *Catal. Today* **2016**, <https://dx.doi.org/10.1016/j.cattod.2016.12.045>.
- [213] S. Sabour, C. Especel, C. Fontaine, M. Bidaoui, L. Benatallan, N. Saib-Bouchenafa, J. B. Jr., O. Mohammedi, *J. Mol. Catal. A: Chem.* **2016**, 420, 50.
- [214] Y. Ide, M. Iwata, Y. Yagenji, N. Tsunoji, M. Sohmiya, K. Komaguchi, T. Sano, Y. Sugahara, *J. Mater. Chem. A* **2016**, 4, 15829.
- [215] K. Brown, S. Zolezzi, P. Aguirre, D. Venegas-Yazigi, V. Paredes-Garcia, R. Baggio, M. A. Novak, E. Spodine, *Dalton Trans.* **2009**, 1422.
- [216] M. Tonigold, Y. Lu, B. Bredenkotter, B. Rieger, S. Bahnmueller, J. Hitzbleck, G. Langstein, D. Volkmer, *Angew. Chem., Int. Ed.* **2009**, 48, 7546.
- [217] K. Leus, I. Muylaert, M. Vandichel, G. B. Marin, M. Waroquier, V. V. Speybroeck, P. V. Der Voort, *Chem. Commun.* **2010**, 46, 5085.
- [218] Y.-Z. Chen, Z. U. Wang, H. Wang, J. Lu, S.-H. Yu, H.-L. Jiang, *J. Am. Chem. Soc.* **2017**, 139, 2035.
- [219] N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin, O. A. Kholdeeva, *Inorg. Chem.* **2010**, 49, 2920.
- [220] X.-L. Yang, L.-M. Qiao, W.-L. Dai, *Microporous Mesoporous Mater.* **2015**, 211, 73.
- [221] J. Zhu, P. C. Wang, M. Lu, *Appl. Catal., A* **2014**, 477, 125.
- [222] K. Leus, P. Concepcion, M. Vandichel, M. Meledina, A. Grirrane, D. Esquivel, S. Turner, D. Poelman, M. Waroquier, V. V. Speybroeck, G. V. Tendeloo, H. García, P. V. D. Voort, *RSC Adv.* **2015**, 5, 22334.
- [223] S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563.
- [224] P. Gallezot, A. Giroir-Fendler, D. Richard, *Catal. Lett.* **1990**, 5, 169.
- [225] S. R. D. Mandal, R. V. Chaudhari, M. Sastry, *Chem. Mater.* **2004**, 16, 3714.
- [226] J. A. R. van Veen, in *Zeolites for Cleaner Technologies* (Eds: M. Guisnet, J.-P. Gilson), Imperial College Press, London, UK **2005**, p. 131.
- [227] I. E. Maxwell, J. K. Minderhoud, W. H. J. Stork, J. A. R. van Veen, in *Handbook of Heterogeneous Catalysis*, Vol. 4 (Eds: G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim, Germany **1997**, p. 2017.
- [228] J. N. Armor, *Appl. Catal.* **1994**, 112, N21.
- [229] J. Heinerman, E. Vogt, *WO94/26846* **1994**.
- [230] A. Corma, A. Martínez, V. Martínez-Soria, *J. Catal.* **1997**, 169, 480.
- [231] L. J. Durndell, C. M. A. Parlett, N. S. Hondow, M. A. Isaacs, K. Wilson, A. F. Lee, *Sci. Rep.* **2015**, 5, 9425.
- [232] G. Liu, J. Wang, T. Huang, X. Liang, Y. Zhang, H. Li, *J. Mater. Chem.* **2010**, 20, 1970.
- [233] J. A. R. Navarro, E. Barea, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, C. O. Ania, J. B. Parra, *Inorg. Chem.* **2006**, 45, 2397.
- [234] F. X. Llabrés i Xamena, A. Abad, A. Corma, H. Garcia, *J. Catal.* **2007**, 250, 294.
- [235] X. Zhang, F. X. Llabrés I Xamena, A. Corma, *J. Catal.* **2009**, 265, 155.
- [236] S. Opelt, S. Turk, E. Dietzsch, A. Henschel, S. Kaskel, E. Klemm, *Catal. Commun.* **2008**, 9, 1286.
- [237] a) J. Hermannsdorfer, M. Friedrich, N. Miyajima, R. Q. Albuquerque, S. Kummel, R. Kempe, *Angew. Chem., Int. Ed.* **2012**, 51, 11473; b) *Angew. Chem.* **2012**, 124, 11640.
- [238] a) Q. Yang, Q. Xu, S. Yu, H. Jiang, *Angew. Chem., Int. Ed.* **2016**, 55, 3685; b) *Angew. Chem.* **2016**, 128, 3749.
- [239] J. M. Falkowski, T. Sawano, T. Zhang, G. Tsun, Y. Chen, J. V. Lockard, W. Lin, *J. Am. Chem. Soc.* **2014**, 136, 5213.