DOI: 10.1002/anie.200806063

Metal–Organic Frameworks: Opportunities for Catalysis

David Farrusseng, Sonia Aguado, and Catherine Pinel*

acid–base catalysis · adsorption · heterogeneous catalysis · metal–organic frameworks · porosity

The role of metal–organic frameworks (MOFs) in the field of catalysis is discussed, and special focus is placed on their assets and limits in light of current challenges in catalysis and green chemistry. Their structural and dynamic features are presented in terms of catalytic functions along with how MOFs can be designed to bridge the gap between zeolites and enzymes. The contributions of MOFs to the field of catalysis are comprehensively reviewed and a list of catalytic candidates is given. The subject is presented from a multidisciplinary point of view covering solid-state chemistry, materials science, and catalysis.

1. Introduction

It is generally acknowledged that metal–organic frameworks (MOFs) exhibit unique and outstanding properties, which have been discussed in various reviews.[1,2] The structural nanoporosity of MOF materials places them at the frontier between zeolites and surface metal–organic catalysts. MOFs therefore appear to be excellent candidates for catalysis, with the understanding of their potential still largely in its infancy.[3,4] Herein we deal comprehensively with MOFs in the field of catalysis, with special focus placed on the design, structure–activity relationships, assets and limits in light of current challenges in catalysis. In addition, an inventory of potentially active MOF materials in catalysis is given.

2. Solid Design by Molecular Approaches

Herein "design" refers to the identification of material architectures that allow the generation of desired functions.

2.1. Self-Assembly and Design by the Building-Block Model

The conceptual approach for MOF engineering is based on the self-assembly of cationic systems acting as nodes with polytopic organic ligands acting as linkers (Figure 1).[5] As an analogy to zeolite frameworks, this secondary building unit (SBU) approach to MOF construction allows the design of specific nanometer-scale framework geometries with particular pore structures. In contrast to zeolites, for which a relatively limited number of structures exists (178 to date), MOFs take advantage of the versatile coordination chemistry, polytopic linkers, and terminating ligands (F^-, OH^-, and H_2O, among others), which makes it possible to design an almost infinite variety of MOF structures. Extensive reviews on MOF structures can be found elsewhere.[6–8]

MOF materials can be classified into different families according to the dimensionality of the inorganic framework (Figure 2):[9] 1) organic–inorganic hybrid materials in which inorganic moieties can be organized into either 1D chains (like MIL-53) or 2D layers (such as Zn_2L) that are separated by organic pillars;[10] and 2) open-framework coordination polymers, which are made from 0D "inorganic" clusters or isolated metal ions connected by bridging organic polytopic ligands (MOP-1, MOF-5, and HKUST-1). This classification is not only conceptual, since it has implications on the properties observed. As demonstrated in Section 3.3, 0D structures are more appropriate for photocatalysis applications and Lewis-type catalysis, whereas 1D may be appropriate for acid–base Brønsted-type catalysis.

2.2. Towards Robust Open, Functionalized, and Sizeable Frameworks

Coordination polymers have been known for decades, but a breakthrough has come from the development of thermally

---

[*] Dr. D. Farrusseng, Dr. S. Aguado, Dr. C. Pinel
Institut de Recherche sur la Catalyse et l'Environnement de Lyon (IRCELYON)
University Lyon 1, CNRSC; 2, Av. Albert Einstein
Villeurbanne, 69626
Fax: (+339) 4-72-44-53-99
E-mail: david.farrusseng@ircelyon.univ-lyon1.fr

stable porous coordination polymers (PCPs) which have permanent porosity and are without guest molecules.[13,14] The "node and spacer" approach is very attractive for shape-selective catalysis because it provides a route to networks with tunable pore size.[8,12] The strategy for increasing the pore size and volume involves the expansion of known structure types through the use of elongated but geometrically equivalent organic bridging ligands. For the IRMOF series based on the MOF-5 structure, the pore size can be varied from 3.8 to 28.8 Å[12] by selecting linkers of various sizes (see Figure 1). Other examples are [Cu(OOC-R-COO)teda] (teda = triethylenediamine),[15] the IRMOP series,[16] the MIL-53 series,[17] the MIL-88 series,[18] the MOF-69 series,[19] $[Cu_2(L_x)(H_2O)_2]$,[20] and UiO-66/68.[21]

The principal weakness of MOFs may lie in their lower thermal, hydrothermal, and chemical stability compared to that of oxides (zeolites). Unfortunately, stability data are usually lacking in the literature. Moreover, when reported, this data is often obtained under different conditions (air or neutral atmosphere, different temperature) and by different means (thermogravimetric analysis (TGA) or thermodiffraction), which makes it impossible to compare the data. Usually, according to TGA, the thermal stability of carboxylate- and imidazolte-based MOFs[22] is limited to 300–400 °C in air (see Supporting Information), though this does leave the door open for most catalytic applications. On the other hand, the chemical stability depends essentially on the cation coordination, provided that the linkers are robust. It is now well established that IRMOF compounds based on Zn_4O clusters are very moisture sensitive and are readily transformed to MOF-69 type, with an accompanying drastic decrease in surface area.[23,24] On the other hand, MIL-53(Al), MIL-100(Fe), MIL-101(Fe), and ZIF-8, -9, -10 are very stable under hydrothermal treatment, whereas *rho*-ZIF-11 undergoes profound structural changes.[25]

David Farrusseng received his BSc in chemistry from the University of Montpellier (France) and his PhD in material science at the European Institute of Membranes (Montpellier) with Drs. A. Julbe and C. Guizard (1999). After a post-doc with Prof. F. Schüth at the MPI für Kohlenforschung (Germany), he joined IRCELYON (2001) where he is a group leader. His research concerns the design of materials for catalytic and separation processes and the development of high-throughput approaches for which he received an awarded from the French Chemical Society (2008).

Sonia Aguado received her PhD (2005) from the University of Zaragoza (Spain). She carried out postdoctoral research in the Catalysis Engineering group of Delft University of Technology (The Netherlands). In 2008, she joined IRCELYON, as a postdoctoral researcher. Her research interests are the synthesis of metal–organic frameworks for catalysis, gas separation, and films.

Catherine Pinel received her PhD in organic chemistry at the University of Paris VI in 1992 under the supervision of Prof. J. P. Genet, then joined the group of Prof. S. V. Ley (University of Cambridge) as a Marie Curie Fellow. Since 1994, she has been developing her research at IRCELYON. Her main scientific interests are the application of heterogeneous catalysts for fine chemistry and the catalytic transformation of biomass.

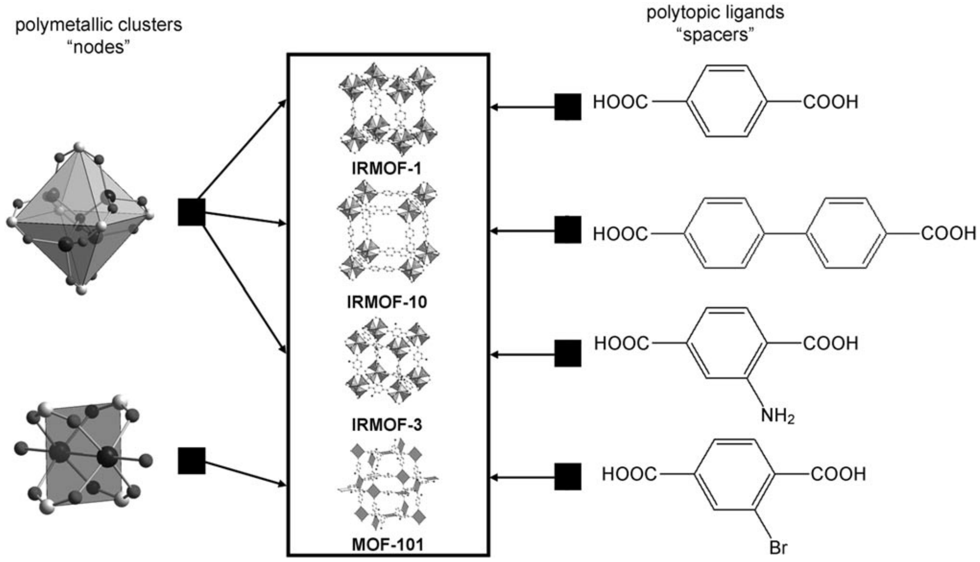

Figure 1. Self-assembly of polymetallic cluster nodes (left; top: μ^4-oxo $\{M_4O(\text{-}CO_2)_6\}$; bottom: $\{M_2(\text{-}CO_2)_4\}$ paddlewheel) and organic linkers (right) yielding metal–organic frameworks (center).[11,12]

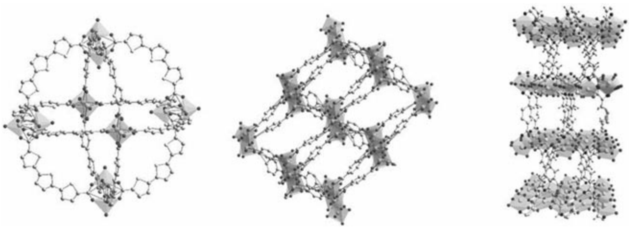

Figure 2. Examples of structural dimensionality. From left to right: 0D (MOP-1), 1D (MIL-53), and 2D (Zn_2L).

2.3. Functionalization Approach and Grafting

The conceptual approach used to increase the pore size of MOFs through the use of longer ligands can be extended to the design of multifunctional MOFs bearing an organic function on the organic moiety. This is the case for IRMOF-3(-NH_2),[12] MOF-101(-Br),[11] and MIL-53(-NH_2),[26] to name a few (see Table 1 in Section 5). This extension is not, however, straightforward in practice.[27,28] Indeed, the chemistry of MOF network formation is very sensitive to the chemical reactivity and solubility of functionalized linkers.[29] This is particularly the case for functions such as -OH, -NH_2, -COOH, and N-donating groups, which can interfere with the coordination chemistry associated with the assembly of the SBU, and thus may lead to non-isostructural compounds. One example of this phenomenon lies in the self-assembly of ZIF, for which even a "minor" change in the ligand composition leads to very different network and pore structure.[30]

When self-assembly fails for the synthesis of MOFs with functional linkers, the post-functionalization of a parent MOF appears to be a very valuable alternative. This approach consists in modifying the organic part of the MOF by a chemical reaction which takes place within the porous framework (Figure 3). In this case, the parent MOF must possess accessible reactive functional groups. Similar issues have been resolved for MCM-like materials, for which various functionalization methods have been developed.[31] In a similar fashion to alkylamine-functionalized MCM, amino-derived MOFs, such as IRMOF-3, are excellent platforms for the grafting of various synthons, such as aldehydes,[32] isocyanates,[33] and anhydride acids.[34] Also noteworthy is the chemical modification of pendant carbonyl groups of ZIF-90 either to imine by amine condensation or to alcohols by $NaBH_4$ reduction.[35] In fact, post-synthesis opens the door to advanced porous solids engineering by multiple synthesis steps[36] and systematic adsorption and catalytic studies dealing with the nature of the functional groups.[34] However, the suitability, diversity, and availability of such synthons is not sufficient for such studies. A valuable alternative lies in the development of all kinds of post-functionalization methods that are soft, do not liberate by-products that may remain blocking the pore, allow the grafting of a wide variety of chemical functions, and are generic enough to allow tailor-made properties to be introduced. Recently, the "click chemistry" method, which concurs with these requirements, was shown to be effective on azide-functionalized MOFs.[37] The question of instability of ungrafted azides nevertheless requires further attention. Also, the size of the generated moiety, with respect to the size of the cavity, must be controlled to avoid pore blockage.

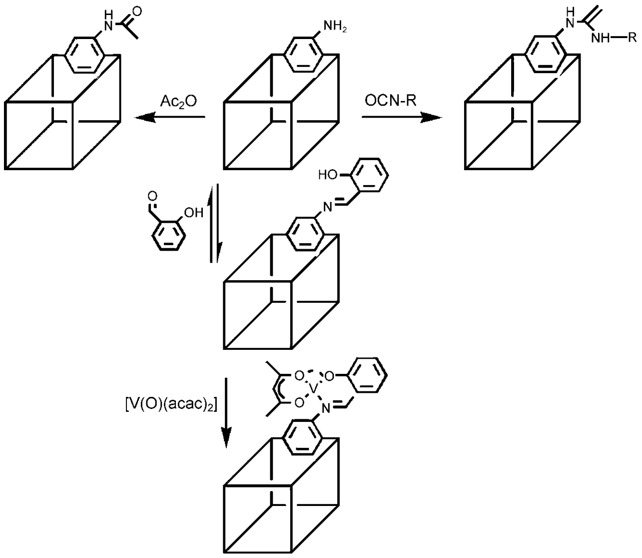

Figure 3. Examples of post-functionalization methods.

3. MOF Materials: Golden Opportunities for Catalysis

In this Section pore structures as well as dynamic properties are described in terms of the required functions for catalysis. Similarities with zeolites and enzymes are highlighted.

3.1. Bridging the Pore Size Gap between Zeolites and Mesoporous Materials

The small pore size of zeolites is usually underlined as a key limitation to addressing the catalytic transformation of large molecules, such as polyaromatics, carbohydrates, and glycerides. Intense efforts have been devoted to the discovery of aluminophosphates and zeolites with very large pores, such as VPI-5,[38] IM-12,[39] and ITQ-33.[40] On the other hand, mesoporous silicate materials, such as MCM-41 have pores too large to impose confinement effects. MOF materials actually bridge the gap between these two porous material types, because MOFs with pore systems ranging from the ultramicroporous to mesoporous have been reported, as shown in the arbitrary selection in Figure 4. The abundant choice of structure which facilitates pore-size tunability is a great opportunity for designing MOFs with pore openings appropriate for generating size and shape selectivity. In addition, the very large cavities of isoreticular MIL-101 (46 Å) can, in principle, address triglycerides and small protein substrates (< 10000 Daltons).[41]

In addition to pore size, analogies between zeolites and MOFs can be found when pore topology is considered. For

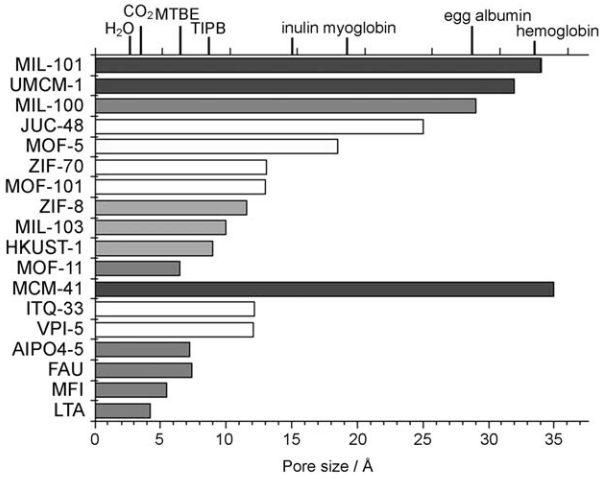

Figure 4. Cavity size of porous MOFs [Å] compared with standard aluminosilicates and aluminophosphates (aluminosilicaltes = MCM-41, ITQ-33, VPI-5, FAU, MFI, LTA, aluminophosphates = AlPO4-5, MOFs = rest). The size of selected potential guests is also shown on the top axis. MTBE = methyl *tert*-butyl ether; TIPB = 1,3,5-triisopropylbenzene. Porous materials shown are selected arbitrarily; pore sizes are approximate because of the variety of pore shapes involved.

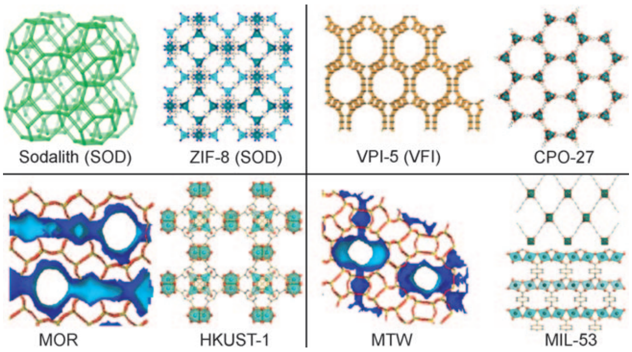

Figure 5. Comparison of porous features between zeolites and MOFs (zeolites = SOD, VPI-5, MOR, MTW; MOFs = ZIF-8, CPO-27, HKUST-1, MIL-53): alpha cages (top left), side pockets (bottom left), 1D straight channels (top right) and 2D porous structures with small intersecting channels (bottom right).

example, the pore structure can be one-dimensional (1D) with straight channels, 2D, or 3D (Figure 5). In addition, as for zeolites, complex porous architecture with large cavities, reduced pore aperture, and side pockets can be observed. A striking example is the HKUST-1 structure consisting of two types of "cages" and two types of "windows" separating these cages.[42] Large cages (13 and 11 Å in diameter) are interconnected by 9 Å windows of square cross-section. The large cages are also connected to tetrahedral-shaped side pockets of roughly 6 Å through triangular-shaped windows of about 4.6 Å. These types of porous architectures are especially appropriate for product-selectivity properties as observed in catalytic alkylation[43] and cracking.[40] Giant cages can be found in imidazole-based MOFs.[44] Examples are the alpha (18.2 Å) and beta cages found in *rho*- and *sod*-ZMOF, respectively.[45] Finally, such topologies are very appropriate for ship-in-a-bottle catalyst design, for which large molecular catalysts, such as metalloporphyrins for selective oxidation, can be encapsulated in the network.[46]

3.2. Towards Biomimetic Design

Well isolated polynuclear clusters in specific flexible and chemical environment are the main features of enzymes. Some MOF materials may bridge the gap between zeolites and enzymes when they combine isolated polynuclear sites, dynamic guest–host responses, and a hydrophobic cavity environment. The three aspects are discussed in the following:

1) Cooperative catalysis involving two metal ions is a common feature in enzymatic systems. The resulting cooperative activation of both reaction partners leads to enhanced reactivity and more specific control, thus making enzymes very powerful catalysts. Some well-known examples of dinuclear and higher nuclearity metal sites in biological systems include: the diiron sites in methane monooxygenase, dicopper in cytochrome *c* oxidase, and tricopper oxidases.[47] By analogy, polynuclear clusters are found in the 0D coordination polymers, such as binuclear $\{Cu_2\}$ paddlewheel [6,48] units found in MOP-1[49,50] and $[Cu_3(btc)_2]$ (HKUST-1; btc = benzene-1,3,5-tricarboxylate) or trinuclear units such as $\{Fe_3O(CO_2)_6\}$ in MIL-88,[18] and IRMOP-51.[16] Thus, 0D MOFs have accessible biomimetic catalytic centers.

2) In enzymatic systems, protein units have a high affinity for specific substrates, a process that is referred to as "molecular recognition." Confining (chiral) substrates within the micropores of solid material can, in principle, induce or enhance (enantio)selectivities beyond those observed in homogeneous solutions. The "locking-in" of a particular configuration of the organometallic complex by entrapment in the restricted spatial environment leads to greater selectivity.[51] It appears that molecular recognition effects are limited in zeolites by the rigid zeolite structure.[52] In contrast, dynamic features and guest-shape response make MOFs more similar to enzymes. Indeed many hybrid frameworks contain organic parts that can rotate as a result of stimuli, such as light and heat.[53] This is the case for frameworks such as IRMOF, MIL-53, and $[Zn_2(1,4\text{-ndc})_2(\text{dabco})]_n$ (ndc = naphthalenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane). For $[Zn_2(1,4\text{-ndc})_2(\text{dabco})]_n$, the aromatic rings are allowed to spin unless an adsorbed guest hinders the rotation through steric effects (Figure 6).[54,55]

In addition some hybrid systems, such as those classified by Kitagawa et al., may exhibit a variety of guest-induced structural phase transitions upon guest adsorption–desorption.[14,54] MIL-53 is a very good illustration of the shrinking or expanding of frameworks according to the polarity of guest molecules. When water or CO_2 is adsorbed, hydrogen bonds are formed with μ_2-OH units of the framework, resulting in a shrinking of the diamond-type channel.[56] In addition to this polarity-response, shape-response fitting has also been observed: The pillar layer compound $[Cu_2(\text{pzdc})_2(\text{bpy})]_n$ (pzdc =

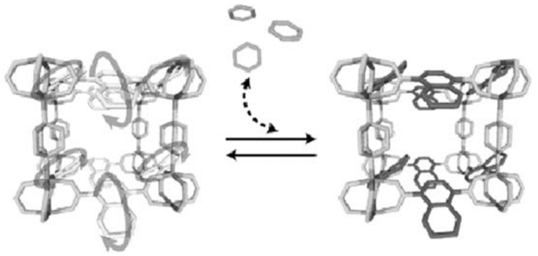

Figure 6. Intrinsic dynamic motion upon input of thermal energy: rotation of naphthalenate linkers between nodes in [Zn_2(1,4-ndc)$_2$(dabco)]$_n$. The rotation is hindered by the incorporation of a guest in the cavity.

pyrazine-2,3-dicarboxylate; bpy = 4,4′-bipyridine), CPL-2, can evolve in response to the shape of the benzene guest molecule resulting in a change of the Cu coordination between square pyramidal and square planar (Figure 7).[57]

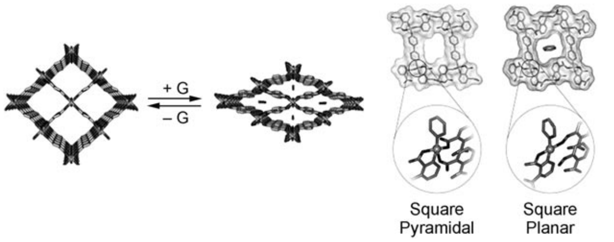

Figure 7. Right: Pore-shape response upon guest (G) adsorption–desorption. Left: these changes can also be accompanied by a change in the coordination geometry of the framework metal centers.

Indeed, it could be anticipated that the shape of the cavity might change upon adsorption, allowing transition-state shape selectivity to take place. A striking example is the activation of acetylene in [Cu_2(pzdc)$_2$(pyz)] (pyz = pyrazine) by a confinement effect arising from a molecular recognition mechanism which is accompanied by structural transformation.[58] This activation by deprotonation makes it possible to carry out the anionic polymerization of acetylene derivates. The straight monodimensional channels (4.0×6.0 Å^2) force the polymerization to proceed by *trans*-addition, which provides very specific product properties.[4]

3) Enzymes are able to select reactants according to polarity and can perform bimolecular reactions between two reactants of very different polarities. It should also be emphasized that enzymes operate in aqueous media thanks to control of water adsorption. Similarly, using the enzymatic model, catalytic efficiency can be enhanced by adjusting the hydrophobicity–hydrophilicity balance of the porous solid.[43] Zeolites containing charges are usually hydrophilic, while defect-free full silica zeolites with no charges are strongly hydrophobic. The hydrophobic nature controls the selectivity of the oxidation of nonpolar hydrocarbons using H_2O_2 as the oxidant.[59] The hydrophobic–hydrophilic properties of a few MOFs have been investigated by water adsorption measurements.[25] HKUST-1 is highly hydrophilic, MIL-101 and MIL-100(Fe) are moderately hydrophilic, whereas ZIF-8 is highly hydrophobic. It might be anticipated that MOF materials exhibiting unsaturated coordinative centers, such as HKUST-1,[60] CPO-27,[61] and others which have recently been reviewed[62] could also be hydrophilic. On the other hand, when the framework contains bridging hydroxy groups as in MIL-53, it creates polar groups that are prone to adsorb H_2O through hydrogen bonding. Unlike zeolites, in MOFs different pore systems with different levels of polarity can coexist within the same structure. For example, [Cu/Pd(pymo)] (pymo = 2-hydroxypyrimidine) exhibits two hexagonal channels: one hydrophilic 4.8 Å channel and one hydrophobic 8.8 Å channel (Figure 8).[63,64] Another MOF with two interpenetrating networks shows two strikingly different chemical environments, with hydrophilic and hydrophobic networks able to selectively adsorb 2-propanol and cyclohexane from a mixture.[65] Finally highly hydrophobic porous MOFs can be obtained by functionalization with a perfluoro moiety.[27,66]

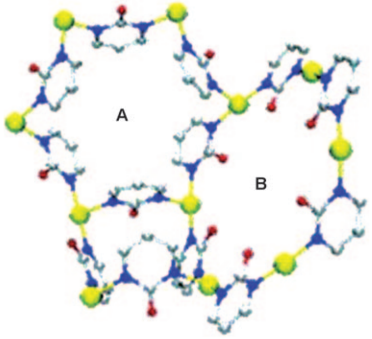

Figure 8. [Cu/Pd(pymo)] exhibiting two types of cavity polarity: A hydrophilic and B hydrophobic. Red O, blue N, yellow Cu/Pd.

3.3. Towards New Photocatalysts

In photocatalysis, the use of mononuclear complexes is usually limited either because they only undergo single-electron process or from the need for high-energy irradiation. More valuable catalysts would adsorb visible photons and be able to participate in the two-electron reactivity needed for H_2 generation. In this case again, binuclear systems have a number of attractive features for the development of photocatalysts.[67] For 0D MOF structures, polycationic nodes can act as semiconductor quantum dots which can be activated upon photostimuli with the linkers serving as photon antennae.[68,69] Theoretical calculations show that MOFs are semiconductors or insulators with band gaps between 1.0 and 5.5 eV which can be altered by changing the degree of conjugation in the ligands.[70] Experimental results show that the band gap (closely related to the HOMO–LUMO gap) of IRMOF-type samples can be tuned by varying the functionality of the linker, whereas the linker length does not have a significant effect.[71] Photo-oxidation examples can be found elsewhere.[66,69,71,72] On the other hand, nanosized TiO_2[73] and ZnO (1.4 nm)[74] can be hosted in MOF-5 to generate new types of quantum-dot materials. Unfortunately, most of the simulation and experimental studies have been carried out on MOF-5. This compound liberates ZnO species (which may become the active species) under humid atmosphere, in the course of the oxidation process,[75] or under thermal treatment ($>250\,°C$).[73] More stable systems should be investigated to evaluate the full potential of MOFs for photocatalytic applications.

4. State of the Art of Catalytic MOFs

4.1. Lewis Acid Catalysis

HKUST-1, which has accessible copper clusters, is an outstanding demonstration of the concept of Lewis acid MOFs.[76,77] The $[Cu_3(btc)_2(H_2O)]$ structure includes a binuclear Cu_2 paddlewheel.[60] The Cu^{2+} ions are connected through a weak bond and the second axial coordination site is filled by a weakly bonded water molecule pointing towards the interior of the cavity. Coordinated water can therefore be easily removed by heat treatment at 383 K, making the Cu Lewis acid center directly accessible to a reactant diffusing within the porous network. Various model reactions for characterizing Lewis acidity were tested: benzaldehyde cyanosilylation,[77] isomerization of alpha-pinene oxide, citronellal cyclization, and rearrangement of ethylene acetal of 2-bromopropiophenone.[76] HKUST-1 was shown to be quite selective, which is typical of hard Lewis acid centers. Although the solid does not show Brønsted sites when properly activated, protic solvents may create Brønsted acidity, which can account for variations in properties when different solvents are used.[78] On the other hand, strongly coordinating solvents, such as THF, can bond the acidic Cu sites and thus prevent Lewis type reactions from taking place.[77]

Lewis acid solids can also perform selective oxidations; for example, Ti-silicate (TS-1) selectively oxidizes alkenes into the corresponding epoxides. Recently, Cu^{2+} trinuclear networks showed high activity and selectivity for the peroxidative oxidation of cyclohexane to the corresponding alcohols and ketones ($MeCN/H_2O/HNO_3$ media).[79] The structure is based on a stable $\{Cu_3(\mu_3\text{-}OH)(\mu\text{-pyrazole})\}$ SBU for which the tetracoordinate metal has readily accessible axial sites. Its activity is comparable to that of the best molecular systems, such as copper and iron complexes (32 % yield and turnover number (TON) of $44\,h^{-1}$). Although the mechanism is still unclear, these trinuclear copper networks are the most efficient catalysts reported to date for the mild peroxidation of alkanes.

4.2. Brønsted Acid Catalysis

Férey and co-workers have reported the catalytic activity of two different MIL-100(Fe, Cr) for Friedel–Crafts benzylation.[80] Despite their identical $[M_3OF_{0.85}(OH)_{0.15}(H_2O)_2(btc)_2]$ structures, the Fe^{3+} catalyst shows much higher catalytic activity the Cr^{3+} catalyst and even surpasses HBEA and HY zeolites. As shown by CO chemisorption at low temperature, MIL-100(Cr^{3+}) shows Cr-OH Brønsted sites of medium acidity and several types of Lewis centers.[78,81] In our group, we have tested 1D MOF materials (rod-shape structure) with structurally well-identified hydroxy centers, namely $[Ga(OH)(bdc)]$ (bdc = benzene-1,4-dicarboxylate) and $[Zn_3(OH)_2(bdc)]$, also known as IM-19 and MOF-69C, respectively.[82] We anticipated that bridging OH groups would generate a Brønsted-type acidity such as that found in the H form of zeolites[43] (Figure 9). IM-19 is the Ga form of the parent structure MIL-53(Ga), which is built from infinite chains of corner-sharing $MO_4(\mu_2\text{-}OH)_2$ ($M = Al^{3+}$, Cr^{3+}),[83] whereas MOF-69C consists of chains of $ZnO_2(OH)_2$ tetrahedron and $ZnO_4(OH)_2$ octahedron with μ_3-OH as the bridging species.[19] IM-19 shows full conversion for toluene terbutylation at 50 °C (TON = $220\,h^{-1}$ at 100 °C),[84] while MOF-69C is very shape selective for the alkylation of large polycyclic aromatics, such as biphenylene.[85] A systematic study of the acid–base properties of this class of 1D MOF is highly desired to determine potential application domains.

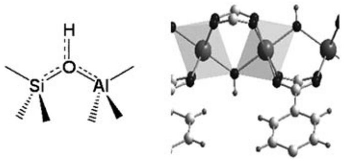

Figure 9. Analogy between a Brønsted acidic site on a H-form zeolite (left) from [43]and a MOF with a bridging hydroxy group between cations in MIL-53 (right).

4.3. Base Catalysis

A few amino-functionalized MOFs have been obtained by direct self-assembly. Solvothermal synthesis using amino-derived ligands, such as 2-aminoterephthalic acid and 3,5-diamino-1,2,4-triazole (Am_2Taz), with zinc yield IRMOF-3, and $[ZnF(Am_2Taz)]$, respectively. IRMOF-3 shows conversion for the Knoevenagel reaction,[86] while IRMOF-3 and $[ZnF(Am_2Taz)]$ are active for Aza-Michael condensations (TON of $1.4\,h^{-1}$ and $0.15\,h^{-1}$, respectively at 25 °C) and fatty methyl ester transesterification (TON = $3.3\,h^{-1}$ and $0.3\,h^{-1}$ at 130 °C).[87] With the exception of POST-1 (a case described below), there are few examples of MOF materials containing free Lewis bases that are accessible for catalytic applications. This might be due to experimental difficulties associate with the synthesis of free-nitrogen-donating MOF materials. Indeed, when nitrogen-containing aromatic moieties in carboxylic-based ligands (such as pyridine/imidazole dicarboxylates[88]) are used, the nitrogen lone pair usually strongly coordinates to the metal ion and is therefore not available for substrate activation. The use of post-functionalization for base catalysis appears to be a valuable alternative (see Section 2.3).

4.4. Enantioselective Catalysis

The design of homochiral MOFs for enantioselective catalysis is of high interest since many useful reactants for chiral transformations are nanometer-sized or larger.[89] To date, however, most homochiral MOFs have not proven sufficiently robust to show permanent porosity, making this topic a continuing challenge.[90] Three strategies have been applied to the synthesis of homochiral MOFs: 1) the use of a rigid homochiral organic ligand as spacer (as with POST-1); 2) the grafting of a homochiral ligand as an auxiliary pendant which does not directly participate in the framework backbone but induces a specific chirality to the structure; and 3) in some cases, the specific orientation of achiral linkers can generate homochiral porous solids.[91]

Enantioselective transesterification was performed with a chiral MOF with free basic centers (POST-1).[92] The self-assembly of the D-tartric acid derivative and Zn^{2+} produces a trinuclear SBU $\{Zn_3(\mu_3\text{-}O)(\text{tartrate})\}$ interconnected through coordinating Zn ions and some pyridyl groups, thereby generating a hexagonal porous system (Figure 10). Other pyridyl groups point toward the center of large 1D chiral channels (13 Å). The ligand chirality induces the structural chirality, selectively leading to D-POST-1 or L-POST-1 materials. The transesterification of dinitrobenzyl acetate with a racemic mixture of 1-phenyl-2-propanol in the presence of D-POST-1 or L-POST-1 produces the corresponding esters with about an 8 % enantiomeric excess in favor of the *S* or *R* enantiomer, respectively.

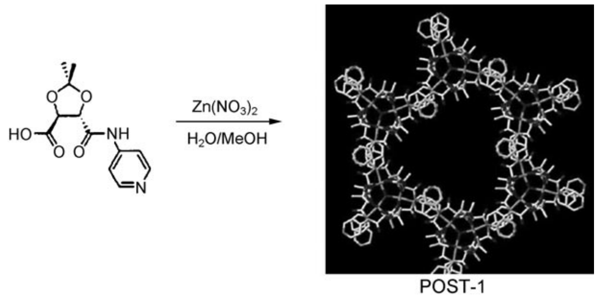

Figure 10. Formation of POST-1.

Examples of grafting molecular catalytic entities onto the walls of a porous network, for example, post-functionalization, are scarce. The homochiral $[Cd_3Cl_6(L_4)_3]\cdot 4\,DMF\cdot 36\,MeOH\cdot H_2O$ (L_4 is (*R*)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphtyl-4,4′-bipyridine) is a 3D network with large chiral channels of about 16 Å × 18 Å and a specific surface area of 601 $m^2\,g^{-1}$.[93] The dihydroxy groups that are readily accessible from the open channels are used to anchor titanium alkoxide units as isolated catalytic sites. The resulting catalyst performs the addition of diethylzinc to 1-naphthaldehyde, leading to (*R*)-1-(1-naphthyl)propanol with complete conversion and 93 % *ee*, which is comparable to results obtained with homogeneous analogues.[94]

4.5. C–C Bond Formation and Polymerization

The $[Pd(2\text{-pymo})_2]\cdot 3\,H_2O$ (2-pymo = 2-hydroxypyridimidolate) material is an outstanding example of MOF material design for catalytic applications.[63] The nodes consist of tetracoordinate palladium ions which are accessible from channels of two different sizes (4.8 Å and 8.8 Å), enabling the activation of substrates to form penta- or hexacoordinate intermediates (see Figure 8). The C–C cross-coupling reaction between aryl halides and arylboronic acids, known as Suzuki–Miyaura coupling, is a benchmark reaction used to rank the activity of palladium catalysts. The palladium-based MOF has a turnover frequency (TOF) of 1230 h^{-1} at 150 °C for this reaction and can be reused without special treatments.

BASF has pioneered polymerization studies with MOFs. Zinc carboxylates have been shown to be active for the polymerization of propylene oxide with CO_2 (20 bar) to yield polycarbonates ($M_W = 60\,000$–$75\,000\ \text{g}\,\text{mol}^{-1}$).[95] Polyols have been obtained by alkoxylation of propylene glycol or acrylic acid with ethylene/propylene oxides on the same type of catalysts.[96] Topotactic radical polymerization of divinylbenzne in the pillared $[M_2(bdc)_2(teda)_n]$ ($M = Zn^{2+}$, Cu^{2+}) can be carried out with 2,2′-azobisisobutyronitrile (AIBN) as the initiator. The 1D porous channel (7.8 Å × 7.8 Å), which imposes constraints on the mobility of the styrene molecules (7.2 Å × 7.2 Å), is responsible for the high selectivity and the very low polydispersity index ($M_w/M_n = 1.6$).[97,98] Outstanding *trans*-selective polymerization of methyl propiolate is obtained in $[Cu_2(pzdc)_2(pyz)_n]$.[4] Short comprehensive reviews can be found elsewhere.[99]

4.6. Nanosized Metallic Particles Supported on MOFs

Because of the very high surface area of MOFs, high metallic dispersion can be expected on such materials, as is the case for carbon-type supports.[100] In addition, the narrow micropore distribution may lead to monodisperse nanometric metallic clusters, which is of high interest for catalytic activity and selectivity. The position of the metallic clusters within the MOF and their size distribution have been investigated by electron microscopy.[100] Chemical vapor infiltration of organometallic precursors was shown to be an appropriate method for obtaining a very high loading (> 30 wt %) of nanosized metal particles, such as Pt, Au, Pd,[74,101] and Ru,[102] into the pores of MOF-5, and MOF-177.[103] The palladium-based catalyst was shown to be active for CO oxidation and cyclooctene hydrogenation. More recently, chemical-based methods were developed to prepare 1 wt % palladium-supported MOF-5 by either incipient wetness impregnation[24] or co-precipitation.[104] Activity superior to Pd/C was observed for the hydrogenation of various alkenes and esters in three-phase reactions.[104] Nanosized Au was hosted in various supports (CPL-1, CPL-2, HKUST-1, MIL-53, and MOF-5) by deposition of $[Me_2Au(acac)]$ followed by mild reduction under H_2 flow (20 % in N_2) at 120 °C.[105] Very narrow gold cluster distribution centered at 1 nm is found for 1 wt % Au/MIL-53(Al). All gold-supported catalysts are active for the aerobic oxidation of benzyl alcohol in methanol. Au/MOF-5 showed the highest catalytic activity for obtaining methyl benzoate, with a yield of 91% at full conversion (TOF = $82\,h^{-1}$ at 80 °C), whereas copper-based MOFs, which are Lewis acids, drive the selectivity toward benzaldehyde. It is suggested that the MOF support affects the gold cluster so that the activation of alcohol is allowed in the absence of a base, in contrast to active carbons. Finally, an advanced synthesis method led to active nanocomposite Cu/ZnO/MOF-5 for methanol synthesis (60% of the activity of a state of the art catalyst), but such solids rapidly degrade on stream.[106]

4.7. Catalysis by Organometallic Complexes Supported on MOFs

5,10,15,20-tetra(carboxyphenyl)porphyrin (tcpp) a porphyrin macrocycle functionalized at its four *meso* positions by 4-carboxyphenyl groups is an extremely versatile building block for the self-assembly of framework solids (Figure 11). Its square planar symmetry with diverging carboxylic functions is perfectly suited for the construction of open quadrangular supramolecular networks.[107,108] A review of coordination polymers using porphyrin functionalized ligand can be found elsewhere.[109] The assembly of tcpp with the paddle-wheel SBU Zn_4O generates a 3D porous MOF (PIZA-4; Langmuir surface = $800\,m^2\,g^{-1}$) that is thermally stable up to 400 °C. It was shown that the hydrophobic–hydrophilic balance of such MOFs is very sensitive to the structure, which in turn depends on the SBU.

Mori et al. have synthesized various rhodium tcpp coordination polymers with dinuclear rhodium paddlewheel nodes.[110,111] They show high activity for the gas-phase hydrogenation of propene. From H_2–D_2 exchange results at 100 K, it was suggested that H_2 is activated on the metalloporphyrin, whereas propene is adsorbed on the rhodium-based node. A similar microporous ruthenium(II,III) complex with porphyrin, $[Ru_2(H_2tcpp)]BF_4$, (H_2TCPP = 4,4′,4′,4-(21H,23H-porphine-5,10,15,20-tetrayl)tetrakis benzoic acid) showed outstanding selectivity for oxidation of primary aliphatic alcohols with air without any additives at room temperature.[112] For example, the oxidation of benzyl alcohol gives the corresponding aldehyde with a selectivity of 95% and a TON of 10 for 24 h of reaction. MOF design was further extended to chiral Mn(salen) struts.[113] The Mn(salen) complex was incorporated through binding of the metal center to pyridine units while biphenyldicarboxylate ligands were used as pillars. The oxidation of 2,2-dimethyl-2*H*-chromene with iodosylbenzene as the oxidant yields an 82% enantiomeric excess, rivaling results obtained with the molecular analogues. Similarly, ligands based on metallo Schiff bases were used to immobilize coordinatively unsaturated metal centers into porous frameworks.[114]

5. Challenges and Outlook

The published studies of catalytic applications using MOF materials generally suffer from a lack of characterization with respect to sample homogeneity and purity. In most cases, only powder X-ray diffraction (XRD) analyses are performed, although low quantities of amorphous metal oxide phases or other crystalline phases present can be responsible for the catalytic activities observed.[76,77] In addition, the homogeneity of samples at short range is usually not investigated, although catalytic phenomena take place at the molecular level. It is indeed well known that structural defects play a major role in catalysis, especially for zeolites.[115] We have observed that structural defects in MOF-5 arising from water sensitivity generate acid sites which can carry out aromatic alkylkation.[116] The building-block approach to MOF construction makes it possible to regard such materials as extended molecules, though they are essentially solids. In this respect, MOFs are quite similar to zeolites, and thus the characterization issues that come with local defects must also be considered.

In light of the structure–activity relationships observed in acid–base catalysis, Table 1 lists MOFs that are potential catalyst candidates, along with a description of their porous structures (dimensionality and pore size).

MOFs are active and selective catalysts for a wide variety of reactions, from acid–base to redox catalysis. They will offer new opportunities for reactions in the field of commodity and speciality products, provided it is possible to tailor not only the nature of the active sites and the dimension/shape of the pores, but also the adsorption properties and local geometry of the active sites. To date, many industrial heterogeneous processes involve acidic zeolites. It is unlikely that MOF materials will replace existing catalysts for mature processes. On the other hand, for many important applications, zeolite pores are too small to target the production of bulky, high added-value molecules. MOFs may therefore play a role in applications involving biomass raw materials, such as terpenes, carbohydrates, fatty methyl esters (FAMEs), and

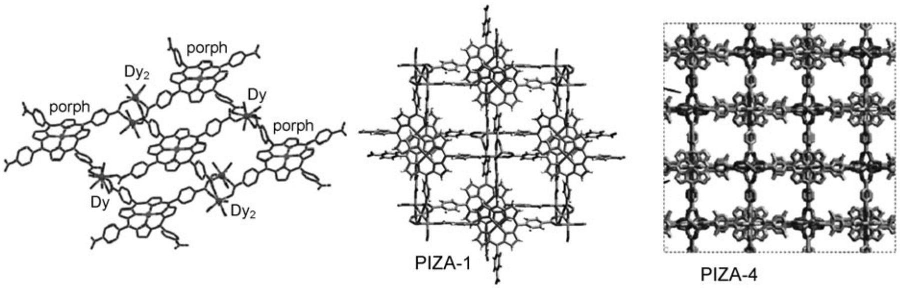

Figure 11. Different MOF structures using porphyrin (porph) carboxylate as linkers; from [107] and [109].

Table 1: Selection of MOF candidates for acid–base or redox catalysis.

Compound[a]	Material name	Metal coordination	Por/inorg[b]	Cavity size [Å]	Acis sites[c]	Basic sites[d]	Ref.
$[\mathrm{Cu_3(btc)_2}]$	HKUST-1	$\{\mathrm{Cu_2O_4}\}$	3D/0D	N/A	L	no	[60]
$[\mathrm{Cu_2(bptc)}]$	MOF-505	$\{\mathrm{Cu_2O_8}\}$	3D/0D	8.3, 10.1	L	no	[118]
$[\mathrm{Zn_2(dhbc)}]$	MOF-74	$\{\mathrm{ZnO_6}\}$	1D/1D	5.5×10.3	B+L	no	[19]
$[\mathrm{V(OH)(bdc)}]_{0.75}$	MIL-47	$\{\mathrm{VO_6}\}$	1D/1D	10.5×11	B	no	[119]
$[\mathrm{M(OH)(bdc)}]_{0.75}$ (M = Al, Cr, Ga)	MIL-53	$\{\mathrm{MO_6}\}$	1D/1D	8.5×8.5	B	no	[2]
$[\mathrm{V(OH)(bdc)}]$	MIL-68	$\{\mathrm{V(OH)_2O_4}\}$	1D/1D	18.6	B	no	[120]
$[\mathrm{Tb(btc)}]$	MIL-103	$\{\mathrm{TbO_9}\}$	1D/1D	10	L	no	[121]
$[\mathrm{M(bdc)}]$ (M = Rh, Cu, Mo)	N/A	N/A	2D/0D	6	L	no	[111]
$[\mathrm{Mg_3(ndc)_3(dmf)_4}]$	TUDMOF-2	$\{\mathrm{Mg_3O_6}\}$	2D/0D	N/A	L	no	[122]
$[\mathrm{Ni_{2.5}(OH)(L\text{-}Asp)_2}]$	N/A	$\{\mathrm{NiO_6}\}$ $\{\mathrm{NiO_5N}\}$	1D/1D	5×8	B	yes	[123]
$[\mathrm{M_2(dhtp)}]$ (M = Co, Ni)	CPO-27 (Ni)	$\{\mathrm{NiO_6}\}$	1D/1D	11	L	no	[61,124]
$[\mathrm{Co_2(bdc)_2(dabco)}]$	N/A	$\{\mathrm{Co_2O_8}\}$	3D/0D	7.6×7.6/5.4	L	no	[125]
$[\mathrm{Mn(ndc)}]$	N/A	$\{\mathrm{MnO_6}\}$	1D/1D	6.1	L	no	[126]
$[\mathrm{Zr_6O_4(OH)_4(CO_2)_{12}}]$	UiO-66/67/68	$\{\mathrm{Zr_6O_6O_{24}}\}$	3D/0D	6/8/10	B	no	[127]
$[\mathrm{Fe(OH)(nbdc)}]$	MIL-53_NH$_2$	$\{\mathrm{MO_6}\}$	1D/1D	N/A	B	yes	[26]
$[\mathrm{M_3(HCOO)_6}]$ (M = Co, Mn, Ni)	N/A	$\{\mathrm{MO_6}\}$	1D/0D	5.5	L	no	[128]
$[\mathrm{Zn_3(NH_2bdc)_3}]$	N/A	$\{\mathrm{Zn_3O_{12}}\}$	1D/0D	N/A	N/A	yes	[129]
$[\mathrm{Cu(bdc)}]$	MOP-1	$\{\mathrm{Cu_2O_8}\}$	3D/0D	15	L	no	[49]
$[\mathrm{M(OH)(bdc)}]$ (M = In, Ga)	MIL-68	$\{\mathrm{MO_4(OH)_2}\}$	1D/1D	6 & 16	B	no	[130]
$[\mathrm{Cr_3XO(bdc)_3}]$ (X = F, OH)	MIL-101	$\{\mathrm{MO_7X}\}$	3D/0D	29 & 34	B+L	no	[131]
$[\mathrm{Fe_3(O)_3Cl(bdc)}]$	MIL-88B_NH$_2$	$\{\mathrm{FeO_6}\}$	1D/1D	N/A		yes	[26]
$[\mathrm{Fe(OH)(NH_2\_nbdc)}]$	MIL-101_NH$_2$	$\{\mathrm{FeO_6}\}$	3D/0D	29 & 34	B	yes	[26]

[a] Coordinated solvent or H_2O molecules have been omitted. [b] Dimensionality of the inorganic part (following Férey's classification) and of the porous structure. [c] Bridging ···OH and coordinatively unsaturated clusters are denoted B (Brønsted) and L (Lewis), respectively. [d] ···NH$_2$ center available. bptc = biphenyltetracarboxylate, dhbc = 2,5-dihydroxybenzoic acid, dhtp = 2,5-dihydroxyterephthalate, nbdc = 2-aminobenzenedicarboxylate.

glycerides. In this case, the successful tailoring of adsorption and diffusion properties will be crucial; porous channels with the appropriate hydrophilic–hydrophobic balance will need to be prepared to achieve the appropriate reactant stoichiometry in the solid. This approach will open the doors to green catalysis using water as the solvent. Finally, homochiral MOFs and photoluminescence properties offer new opportunities for enantioselective catalysis and photocatalysis, domains in which zeolites have met limited success.[117]

MOF materials are dream compounds for catalysis because 1) they can be designed on a rational basis and 2) site isolation allows the assessment of structure–activity relationships. The tunability, versatility, and original flexibility of MOFs make them unique, placing them at the frontier between zeolites and enzymes. The combination of different functions will allow complex cascade reactions and concerted mechanisms to an extent that cannot yet be anticipated, opening great new roads to discovery.

We thank the European Community, TOPCOMBI project (NMP2-CT2005-515792) and IFP for financial support. We also thank Dr. Claude Mirodatos, Dr. Pierre Gallezot, and Dr. Patricia Denton for helpful discussions regarding this manuscript.

Received: December 12, 2008
Revised: March 14, 2009
Published online: August 18, 2009

---

[1] a) S. Natarajan, S. Mandal, *Angew. Chem.* **2008**, *120*, 4876; *Angew. Chem. Int. Ed.* **2008**, *47*, 4798; b) R. E. Morris, P. S. Wheatley, *Angew. Chem.* **2008**, *120*, 5044; *Angew. Chem. Int. Ed.* **2008**, *47*, 4966; c) D. Maspoch, D. Ruiz-Molina, J. Veciana, *Chem. Soc. Rev.* **2007**, *36*, 770; d) C. Janiak, *Dalton Trans.* **2003**, 2781; e) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, *J. Mater. Chem.* **2006**, *16*, 626.

[2] G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191.

[3] G. Férey, *Actual. Chim.* **2007**, 304.

[4] T. Uemura, R. Kitaura, Y. Ohta, M. Nagaoka, S. Kitagawa, *Angew. Chem.* **2006**, *118*, 4218; *Angew. Chem. Int. Ed.* **2006**, *45*, 4112.

[5] a) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474; b) 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; c) J. Kim, B. L. Chen, T. M. Reineke, H. L. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239; d) M. O'Keeffe, M. Eddaoudi, H. L. Li, T. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3; e) G. Férey, *J. Solid State Chem.* **2000**, *152*, 37; f) M. W. Hosseini, *Acc. Chem. Res.* **2005**, *38*, 313.

[6] J. L. C. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.* **2004**, *73*, 3.

[7] a) M. J. Rosseinsky, *Microporous Mesoporous Mater.* **2004**, *73*, 15; b) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; c) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466; d) F. Schüth, K. S. W. Sing, J. Weitkamp, *Handbook of Porous Solids*, *Vol. 2*, Wiley-VCH, **2002**; e) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268.

[8] N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *CrystEngComm* **2002**, *4*, 401.
[9] G. Férey, *Chem. Mater.* **2001**, *13*, 3084.
[10] X. Lin, A. J. Blake, C. Wilson, X. Z. Sun, N. R. Champness, M. W. George, P. Hubberstey, R. Mokaya, M. Schröder, *J. Am. Chem. Soc.* **2006**, *128*, 10745.
[11] M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376.
[12] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.
[13] S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739.
[14] S. Kitagawa, K. Uemara, *Chem. Soc. Rev.* **2005**, *34*, 109.
[15] K. Seki, W. Mori, *J. Phys. Chem. B* **2002**, *106*, 1380.
[16] A. C. Sudik, A. R. Millward, N. W. Ocking, A. P. Cote, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110.
[17] a) T. Loiseau, C. Mellot-Draznieks, H. Muguerra, G. Férey, M. Haouas, F. Taulelle, *C. R. Chim.* **2005**, *8*, 765; b) I. Senkovska, F. Hoffmann, M. Fröba, J. Getzschmann, W. Böhlmann, S. Kaskel, *Microporous Mesoporous Mater.* **2009**, DOI: 10.1016/j.micromeso.2009.02.020.
[18] S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millange, G. Férey, *Chem. Commun.* **2006**, 284.
[19] N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504.
[20] X. Lin, J. Jia, X. Zhao, M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey, M. Schröder, *Angew. Chem.* **2006**, *118*, 7518; *Angew. Chem. Int. Ed.* **2006**, *45*, 7358.
[21] J. Hafizovic, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.* **2008**, *130*, 13850.
[22] K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186.
[23] a) S. Hausdorf, F. Baitalow, J. Seidel, F. Mertens, *J. Phys. Chem. A* **2007**, *111*, 4259; b) S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 14176; c) K. Schröck, F. Schroder, M. Heyden, R. A. Fischer, M. Havenith, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4732.
[24] M. Sabo, A. Henschel, H. Froede, E. Klemm, S. Kaskel, *J. Mater. Chem.* **2007**, *17*, 3827.
[25] P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, S. Kaskel, *Microporous Mesoporous Mater.* **2009**, *120*, 325.
[26] S. Bauer, C. Serre, T. Devic, P. Horcajada, J. Marrot, G. Férey, N. Stock, *Inorg. Chem.* **2008**, *47*, 7568.
[27] C. Yang, X. P. Wang, M. A. Omary, *J. Am. Chem. Soc.* **2007**, *129*, 15454.
[28] M. Kawano, T. Kawamichi, T. Haneda, T. Kojima, M. Fujita, *J. Am. Chem. Soc.* **2007**, *129*, 15418.
[29] R. A. Fischer, C. Wöll, *Angew. Chem.* **2008**, *120*, 8285; *Angew. Chem. Int. Ed.* **2008**, *47*, 8164.
[30] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939.
[31] A. P. Wright, M. E. Davis, *Chem. Rev.* **2002**, *102*, 3589.
[32] M. J. Ingleson, J. P. Barrio, J. B. Guilbaud, Y. Z. Khimyak, M. J. Rosseinsky, *Chem. Commun.* **2008**, 2680.
[33] E. Dugan, Z. Q. Wang, M. Okamura, A. Medina, S. M. Cohen, *Chem. Commun.* **2008**, 3366.
[34] K. K. Tanabe, Z. Q. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2008**, *130*, 8508.
[35] W. Morris, C. J. Doonan, H. Furukawa, R. Banerjee, O. M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 12626.
[36] Z. Wang, S. M. Cohen, *Angew. Chem.* **2008**, *120*, 4777; *Angew. Chem. Int. Ed.* **2008**, *47*, 4699.
[37] Y. Goto, H. Sato, S. Shinkai, K. Sada, *J. Am. Chem. Soc.* **2008**, *130*, 14354.
[38] M. E. Davis, C. Saldarriaga, C. Montes, J. Garces, C. Crowder, *Zeolites* **1988**, *8*, 362.
[39] J. L. Paillaud, B. Harbuzaru, J. Patarin, N. Bats, *Science* **2004**, *304*, 990.
[40] A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, C. Martinez, M. Moliner, *Nature* **2006**, *443*, 842.
[41] A. Sonnauer, F. Hoffmann, M. Froeba, L. Kienle, V. Duppel, M. Thommes, C. Serre, G. Férey, N. Stock, *Angew. Chem.* **2009**, DOI: 10.1002/ange.200805980; *Angew. Chem. Int. Ed.* **2009**, DOI: 10.1002/anie.200805980.
[42] a) C. Chmelik, J. Kaerger, M. Wiebcke, J. Caro, J. M. van Baten, R. Krishna, *Microporous Mesoporous Mater.* **2008**, *117*, 22; b) J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304.
[43] A. Corma, *J. Catal.* **2003**, *216*, 298.
[44] B. Wang, A. P. Cote, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nature* **2008**, *453*, 207.
[45] Y. Liu, V. Kravtsov, R. Larsen, M. Eddaoudi, *Chem. Commun.* **2006**, 1488.
[46] M. H. Alkordi, R. Larsen, J. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 12639.
[47] E. I. Solomon, A. J. Augustine, J. Yoon, *Dalton Trans.* **2008**, 3921.
[48] S. Vagin, A. Ott, B. Rieger, *Chem. Ing. Tech.* **2007**, *79*, 767.
[49] M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 4368.
[50] a) Z. Ni, A. Yassar, T. Antoun, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 12752; b) H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 11650.
[51] M. E. Davis, *Microporous Mesoporous Mater.* **1998**, *21*, 173.
[52] T. F. Degnan, *J. Catal.* **2003**, *216*, 32.
[53] a) A. Kuc, A. Enyashin, G. Seifert, *J. Phys. Chem. B* **2007**, *111*, 8179; b) E. Y. Lee, S. Y. Jang, M. P. Suh, *J. Am. Chem. Soc.* **2005**, *127*, 6374.
[54] S. Bureekaew, S. Shimomura, S. Kitagawa, *Sci. Technol. Adv. Mater.* **2008**, *9*, 014108.
[55] S. Horike, R. Matsuda, D. Tanaka, R. Matsuda, M. Mizuno, K. Endo, S. Kitagawa, *Angew. Chem.* **2006**, *118*, 7384; *Angew. Chem. Int. Ed.* **2006**, *45*, 7226.
[56] F. Coudert, M. Jeffroy, A. H. Fuchs, A. Boutin, C. Mellot-Draznieks, *J. Am. Chem. Soc.* **2008**, *130*, 14294.
[57] a) Y. Kubota, M. Takata, R. Matsuda, S. Kitagawa, T. Kobayashi, *Angew. Chem.* **2006**, *118*, 5054; *Angew. Chem. Int. Ed.* **2006**, *45*, 4932; b) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, S. Horike, M. Takata, *J. Am. Chem. Soc.* **2004**, *126*, 14063.
[58] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. Belosludov, T. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238.
[59] A. Corma, M. 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.
[60] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.
[61] P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom, H. Fjellvag, *Chem. Commun.* **2006**, 959.
[62] M. Dincă, J. R. Long, *Angew. Chem.* **2008**, *120*, 6870; *Angew. Chem. Int. Ed.* **2008**, *47*, 6766.
[63] F. Xamena, A. Abad, A. Corma, H. Garcia, *J. Catal.* **2007**, *250*, 294.
[64] F. Xamena, O. Casanova, R. Galiasso Tailleur, H. Garcia, A. Corma, *J. Catal.* **2008**, *255*, 220.
[65] M. Kawano, T. Kawamichi, T. Haneda, T. Kojima, M. Fujita, *J. Am. Chem. Soc.* **2007**, *129*, 15418.
[66] F. Gándara, A. de Andres, B. Gomez-Lor, E. Gutierrez-Puebla, M. Iglesias, M. A. Monge, D. M. Proserpio, N. Snejko, *Cryst. Growth Des.* **2008**, *8*, 378.
[67] A. Esswein, D. Nocera, *Chem. Rev.* **2007**, *107*, 4022.

[68] a) S. Bordiga, C. Lamberti, G. Ricchiardi, L. Regli, F. Bonino, A. Damin, K. P. Lillerud, M. Bjorgen, A. Zecchina, *Chem. Commun.* **2004**, 2300; b) C. Yang, M. Messerschmidt, P. Coppens, M. A. Omary, *Inorg. Chem.* **2006**, *45*, 6592.

[69] F. Llabrés i Xamena, A. Corma, H. Garcia, *J. Phys. Chem. C* **2007**, *111*, 80.

[70] a) M. Fuentes-Cabrera, D. M. Nicholson, B. G. Sumpter, M. Widom, *J. Chem. Phys.* **2005**, *123*, 124713; b) B. Civalleri, F. Napoli, Y. Noel, C. Roetti, R. Dovesi, *CrystEngComm* **2006**, *8*, 364; c) A. Kuc, A. Enyashin, G. Seifert, *J. Phys. Chem. B* **2007**, *111*, 8179.

[71] J. Gascon, M. D. Hernández-Alonso, A. R. Almeida, G. P. M. van Klink, F. Kapteijn, G. Mul, *ChemSusChem* **2008**, *1*, 981.

[72] a) M. Alvaro, E. Carbonell, B. Ferrer, F. Xamena, H. Garcia, *Chem. Eur. J.* **2007**, *13*, 5106; b) P. Mahata, G. Madras, S. Natarajan, *J. Chem. Phys.* **2006**, *110*, 13759.

[73] M. Müller, X. N. Zhang, Y. M. Wang, R. A. Fischer, *Chem. Commun.* **2009**, 119.

[74] S. Hermes, F. Schröder, S. Amirjalayer, R. Schmid, R. A. Fischer, *J. Mater. Chem.* **2006**, *16*, 2464.

[75] J. Hafizovic, M. Bjorgen, U. Olsbye, P. D. C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti, K. P. Lillerud, *J. Am. Chem. Soc.* **2007**, *129*, 3612.

[76] L. Alaerts, E. Seguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs, D. E. De Vos, *Chem. Eur. J.* **2006**, *12*, 7353.

[77] K. Schlichte, T. Kratzke, S. Kaskel, *Microporous Mesoporous Mater.* **2004**, *73*, 81.

[78] A. Vimont, J. M. Goupil, J. C. Lavalley, M. Daturi, S. Surble, C. Serre, F. Millange, G. Férey, N. Audebrand, *J. Am. Chem. Soc.* **2006**, *128*, 3218.

[79] C. Di Nicola, Y. Y. Karabach, A. M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, *Inorg. Chem.* **2007**, *46*, 221.

[80] P. Horcajada, S. Surble, C. Serre, D. Y. Hong, Y. K. Seo, J. S. Chang, J. M. Greneche, I. Margiolaki, G. Férey, *Chem. Commun.* **2007**, 2820.

[81] A. Vimont, H. Leclerc, F. Mauge, M. Daturi, J. C. Lavalley, S. Surble, C. Serre, G. Férey, *J. Phys. Chem. C* **2007**, *111*, 383.

[82] N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **2002**, *114*, 294; *Angew. Chem. Int. Ed.* **2002**, *41*, 284.

[83] F. Millange, C. Serre, G. Férey, *Chem. Commun.* **2002**, 822.

[84] U. Ravon, M. Savonnet, D. Farrusseng, A. Simon-Masseron, G. Chaplais, D. Bazer-Bachi, N. Bats, V. Lecocq, FR 0805536, **2008**.

[85] U. Ravon, M. Savonnet, S. Aguado, M. E. Domine, D. Farrusseng, *Microporous Mesoporous Mater.*, **2009**, doi:10.1016/j.micromeso.2009.06.008.

[86] J. Gascon, M. D. Hernandez-Alonso, A. R. Ameida, G. P. M. van Klink, F. Kapteijn, G. Mul, *J. Catal.* **2009**, *261*, 75.

[87] M. Savonnet, U. Ravon, S. Aguado, D. Bazer-Bachi, V. Lecocq, N. Bats, C. Pinel, D. Farrusseng, *Green Chem.* **2009**, DOI: 10.1039/b915291c.

[88] H. Hayashi, A. P. Cote, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nat. Mater.* **2007**, *6*, 501.

[89] M. E. Davis, *Nature* **2002**, *417*, 813.

[90] a) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273; b) D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2004**, *126*, 6106; c) C. J. Kepert, T. J. Prior, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2000**, *122*, 5158; d) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1998**, 31.

[91] W. Li, Z. F. Ju, Q. X. Yao, J. Zhang, *CrystEngComm* **2008**, *10*, 1325.

[92] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982.

[93] a) C. D. Wu, A. Hu, L. Zhang, W. B. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940; b) C. D. Wu, W. B. Lin, *Chem. Commun.* **2005**, 3673; c) W. B. Lin, *J. Solid State Chem.* **2005**, *178*, 2486.

[94] C. Wu, W. Lin, *Angew. Chem.* **2007**, *119*, 1093; *Angew. Chem. Int. Ed.* **2007**, *46*, 1075.

[95] U. Mueller, G. Luinstra, O. M. Yaghi (BASF AG, University of Michigan), US 6617467, **2003**.

[96] U. Mueller, M. Stober, R. Ruppel, E. Baum, E. Bohres, M. Sigi, L. Lobree, O. M. Yaghi, M. Eddaoudi, (BASF AG, University of Michigan), PL370429, **2003**.

[97] T. Uemura, D. Hiramatsu, Y. Kubota, M. Takata, S. Kitagawa, *Angew. Chem.* **2007**, *119*, 5075; *Angew. Chem. Int. Ed.* **2007**, *46*, 4987.

[98] T. Uemura, K. Kitagawa, S. Horike, T. Kawamura, S. Kitagawa, M. Mizuno, K. Endo, *Chem. Commun.* **2005**, 5968.

[99] a) S. Kitagawa, D. Tanaka, *Chem. Mater.* **2008**, *20*, 922; b) T. Uemura, S. Horike, S. Kitagawa, *Chem. Asian J.* **2006**, *1*, 36.

[100] S. Turner, O. I. Lebedev, F. Schröder, D. Esken, R. A. Fischer, G. Van Tendeloo, *Chem. Mater.* **2008**, *20*, 5622.

[101] S. Hermes, M. K. Schroter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer, R. A. Fischer, *Angew. Chem.* **2005**, *117*, 6394; *Angew. Chem. Int. Ed.* **2005**, *44*, 6237.

[102] F. Schröder, D. Esken, M. Cokoja, M. W. E. van den Berg, O. I. Lebedev, G. Van Tendeloo, B. Walaszek, G. Buntkowsky, H.-H. Limbach, B. Chaudret, R. A. Fischer, *J. Am. Chem. Soc.* **2008**, *130*, 6119.

[103] M. Muller, O. I. Lebedev, R. A. Fischer, *J. Mater. Chem.* **2008**, *18*, 5274.

[104] S. Opelt, S. Turk, E. Dietzsch, A. Henschel, S. Kaskel, E. Klemm, *Catal. Commun.* **2008**, *9*, 1286.

[105] T. Ishida, M. Nagaoka, T. Akita, M. Haruta, *Chem. Eur. J.* **2008**, *14*, 8456.

[106] M. Muller, S. Hermes, K. Kaehler, M. W. E. van den Berg, M. Muhler, R. A. Fischer, *Chem. Mater.* **2008**, *20*, 4576.

[107] S. George, S. Lipstman, I. Golberg, *Cryst. Growth Des.* **2006**, *6*, 2651.

[108] a) I. Goldberg, *Chem. Commun.* **2005**, 1243; b) M. Shmilovits, Y. Diskin-Posner, M. Vinodu, I. Golberg, *Cryst. Growth Des.* **2003**, *3*, 855.

[109] K. S. Suslick, P. Bhyrappa, J. H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry, S. R. Wilson, *Acc. Chem. Res.* **2005**, *38*, 283.

[110] W. Mori, S. Takamizawa, C. N. Kato, T. Ohmura, T. Sato, *Microporous Mesoporous Mater.* **2004**, *73*, 31.

[111] W. Mori, T. Sato, T. Ohmura, C. N. Kato, T. Takei, *J. Solid State Chem.* **2005**, *178*, 2555.

[112] a) C. N. Kato, M. Ono, T. Hino, T. Ohmura, W. Mori, *Catal. Commun.* **2006**, *7*, 673; b) C. N. Kato, W. Mori, *C. R. Chim.* **2007**, *10*, 284.

[113] S. H. Cho, B. Q. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563.

[114] a) S. Noro, H. Miyasaka, S. Kitagawa, T. Wada, T. Okubo, M. Yamashita, T. Mitani, *Inorg. Chem.* **2005**, *44*, 133; b) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. Noro, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 2738; *Angew. Chem. Int. Ed.* **2004**, *43*, 2684.

[115] M. A. Camblor, A. Corma, S. Iborra, S. Miquel, J. Primo, S. Valencia, *J. Catal.* **1997**, *172*, 76.

[116] U. Ravon, M. E. Domine, C. Gaudillère, A. Desmartin-Chomel, D. Farrusseng, *New J. Chem.* **2008**, *32*, 937.

[117] S. B. Ogunwumi, T. Bein, *Chem. Commun.* **1997**, 901.

[118] B. L. Chen, N. W. Ockwig, F. R. Fronczek, D. S. Contreras, O. M. Yaghi, *Inorg. Chem.* **2005**, *44*, 181.

[119] K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem.* **2002**, *114*, 291; *Angew. Chem. Int. Ed.* **2002**, *41*, 281.

[120] K. Barthelet, J. Marrot, G. Férey, D. Riou, *Chem. Commun.* **2004**, 520.

[121] T. Devic, C. Serre, N. Audebrand, J. Marrot, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 12788.
[122] I. Senkovska, S. Kaskel, *Eur. J. Inorg. Chem.* **2006**, 4564.
[123] E. V. Anokhina, Y. B. Go, Y. Lee, T. Vogt, A. J. Jacobson, *J. Am. Chem. Soc.* **2006**, *128*, 9957.
[124] P. D. C. Dietzel, Y. Morita, R. Blom, H. Fjellvag, *Angew. Chem.* **2005**, *117*, 6512; *Angew. Chem. Int. Ed.* **2005**, *44*, 6354.
[125] H. Wang, J. Getzschmann, I. Senkovska, S. Kaskel, *Microporous Mesoporous Mater.* **2008**, *116*, 653.
[126] H. R. Moon, N. Kobayashi, M. P. Suh, *Inorg. Chem.* **2006**, *45*, 8672.
[127] J. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. Lillerud, *J. Am. Chem. Soc.* **2008**, *130*, 13850.
[128] K. Li, D. H. Olson, J. Lee, W. Bi, K. Wu, T. Yuen, Q. Xu, J. Li, *Adv. Funct. Mater.* **2008**, *18*, 2205.
[129] X. Wang, Y. Zhang, X. Cheng, X. Chen, *CrystEngComm* **2008**, *10*, 753.
[130] C. Volkringer, M. Meddouri, T. Loiseau, N. Guillou, J. Marrot, G. Férey, M. Haouas, F. Taulelle, N. Audebrand, M. Latroche, *Inorg. Chem.* **2008**, *47*, 11892.
[131] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040.