Porous Materials

DOI: 10.1002/anie.200705998

Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation**

Young Kyu Hwang, Do-Young Hong, Jong-San Chang, Sung Hwa Jhung, You-Kyong Seo, Jinheung Kim, Alexandre Vimont, Marco Daturi, Christian Serre, and Gérard Férey**

In porous catalysts,[1] the existence of coordinatively unsaturated metal sites (CUSs) is very beneficial.[2] For instance, these sites allow strong interactions with trapped gases and grafting of organic molecules.[3] Among them, amines with an alkoxysilane functional group are often used, particularly with mesoporous silicas for their applications in base-catalyzed reactions[4] and the immobilization and encapsulation of large molecules,[5] but hydroxy groups on the surface are required. Besides mesoporous solids with amorphous walls, crystallized metal–organic frameworks (MOFs),[6] which are well known for their applications in gas storage,[7] separation,[8] catalysis,[9] and drug delivery[10] can provide a useful alternative for the introduction of functional groups.

These solids result from the tight association of inorganic and organic parts to build up open frameworks and the inorganic moieties can sometimes generate CUSs which, owing to the regular arrangements and well-understood surrounding environments of metal centers in the pore channels, could be used to induce regioselectivity and shape- or size-selectivity towards guest molecules or reaction intermediates.[11] Chui et al. reported that the channel linings of a porous metal coordination polymer can be chemically functionalized; for example, the aqua ligands can be replaced by pyridine.[2c] Post-synthetic modification of a ligand in IRMOF-3 was covalently funtionalized by acetylation.[12] Importantly, Kitagawa and co-workers have proposed two smart strategies on this point, that is, immobilization of CUSs[13a] and introduction of functional organic sites[13b] to decorate channel surfaces of coordination polymers, but these strategies include only the functionalization of the ligand and incorporation of low-coordination metal centers in the primary synthesis. The challenge was then to establish a new and facile method for the surface grafting of porous hybrid materials to facilitate their applications.

Chromium(III) terephthalate MIL-101[14] or $Cr_3(F,OH)(H_2O)_2O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3\cdot n\,H_2O$ ($n \approx 25$), was chosen for this strategy. It has two types of zeotypic mesoporous pores (Figure 1 A) with free diameters of ca. 29 and 34 Å accessible through two microporous windows of ca. 12 and 16 Å, very large BET (Brunauer–Emmett–Teller)and Langmuir surface areas ($4100 \pm 200\ m^2\,g^{-1}$; $5900 \pm 300\ m^2\,g^{-1}$), and numerous potential unsaturated chromium sites (up to 3.0 mmol g^{-1}).

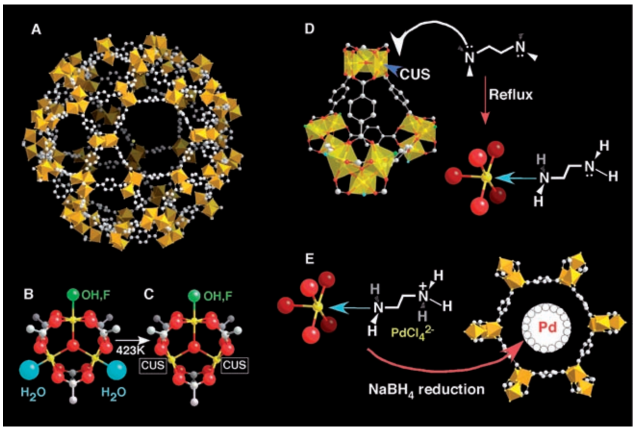


Figure 1. Site-selective functionalization of MIL-101 with unsaturated metal sites: A) perspective view of the mesoporous cage of MIL-101 with hexagonal windows; B,C) evolution of coordinatively unsaturated sites from chromium trimers in mesoporous cages of MIL-101 after vacuum treatment at 423 K for 12 h; D) surface functionalization of the dehydrated MIL-101 through selective grafting of amine molecules (i.e. ethylenediamine) onto coordinatively unsaturated sites; E) selective encapsulation of noble metals in the amine-grafted MIL-101 via a three-step process (see text). Chromium atoms/octahedra yellow, carbon atoms pale gray, oxygen atoms red.

---

[*] Dr. Y. K. Hwang, Dr. D.-Y. Hong, Dr. J.-S. Chang, Prof. S. H. Jhung, Y.-K. Seo
Catalysis Center for Molecular Engineering
Korea Research Institute of Chemical Technology (KRICT)
Jang-dong 100, Yuseong, 305-600 Daejon (Korea)
Fax: (+82) 428-607-676
E-mail: jschang@krict.re.kr

Prof. S. H. Jhung
Department of Chemistry
Kyungpook National University
Daegu 702-701 (Korea)

Dr. C. Serre, Prof. G. Férey
Institut Lavoisier (UMR CNRS 8180)
Université de Versailles Saint-Quentin-en-Yvelines
45 avenue des Etats-Unis, 78035 Versailles cedex (France)
Fax: (+33) 13-925-4379
E-mail: ferey@chimie.uvsq.fr

Dr. A. Vimont, Dr. M. Daturi
Laboratoire Catalyse et Spectrochimie, UMR 6506
CNRS/ENSICAEN et Université de Caen Basse-Normandie
UNICITE 14, rue Alfred Kastler, 14052 Caen Cedex 4 (France)

Prof. J. Kim
Department of Chemistry, Division of Nano Sciences
Ewha Womans University
Seoul 120-750 (Korea)

[**] This work was supported by MOCIE through the Research Center for Nanocatalysts (TS-071-06), Institutional Research Program (KK-0803-E0), and partially the SRC/ERC program of MOST/KOSEF (R11-2005-0008-00000-0 to J.K.). The Korean partners are grateful to EnG Tech Co., Ltd. for the financial support. The French partners are grateful to CNRS for the financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Indeed, trimeric chromium(III) octahedral clusters of MIL-101 possess terminal water molecules, removable from the framework after vacuum treatment at 423 K for 12 h, thus providing the CUS as Lewis acid sites in the structure[2d,3a] usable for the surface functionalization (Figure 1 B,C). Thus we present herein a new method for direct and selective coordination of electron-rich functional groups to CUSs in MOFs and examine its catalytic consequences.

MIL-101 was hydrothermally synthesized at 493 K for 8 h with a cooling ramp down to room temperature for 3 h.[14a] The as-synthesized MIL-101 was further purified by three-step processes using hot ethanol and aqueous NH_4F solutions (see the Supporting Information). After purification of the as-synthesized solid, which contains occluded terephthalic acid, and activation (423 K, 12 h), in situ IR spectroscopic analysis of the dehydrated MIL-101 upon CO adsorption reveals 1.0 mmol$\,g^{-1}$ of chromium(III) CUSs in the framework, indicating the presence of residual terephthalic acid coordinated to a CUS (Figure 2 b). For the selective functionalization of CUSs, we chose first an effective grafting reagent with multifunctional chelating groups, that is, ethylenediamine (ED). As illustrated in Figure 1 D, if one amine group of ED is linked to a CUS of chromium(III) of MIL-101 by direct ligation, the other amine group can play the role of immobilized base catalyst. Clearly, this concept does not apply to the surface functionalization of mesoporous silicas owing to their lack of the unsaturated surface sites in general (see the Supporting Information, Figure S1).

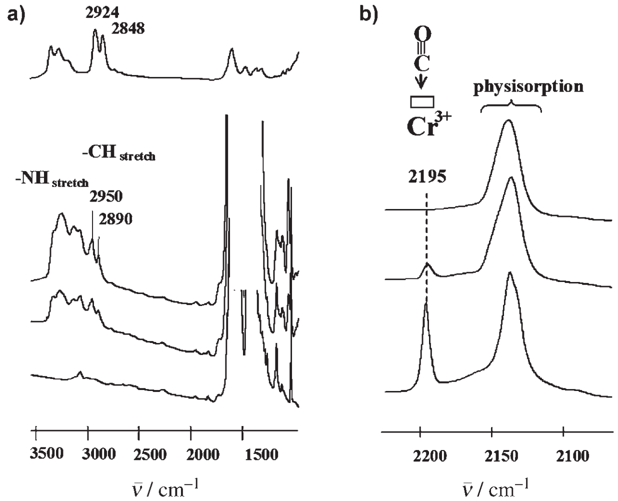


Figure 2. Infrared spectra of the grafted catalysts and chromium CUS characterization: a) Infrared spectra of (bottom) MIL-101, ED-MIL-101, and ED-MIL-101(D) outgassed at 423 K, and (top) of ED in the liquid phase shown for comparison. b) Infrared spectra recorded at 100 K of MIL-101 (bottom), ED-MIL-101 (middle), and ED-MIL-101(D) (top) outgassed at 473 K after introduction of an equilibrium pressure (200 Pa) of CO.

The synthesis of the ED-grafted MIL-101 (ED-MIL-101) by coordination of ED to the dehydrated MIL-101 framework was performed in toluene by heating to reflux. Diethylenetriamine (DETA) and 3-aminopropyltrialkoxysilane (APS) can also be used for the surface functionalization.

The almost unchanged X-ray diffraction patterns show that the ED grafting occurs with no apparent loss of crystallinity (see the Supporting Information, Figure S2), but with some slight variations of the Bragg intensities. The IR spectra of the self-supported ED-MIL-101 and ED-MIL-101(D) wafers (D indicates a double amount of grafting) dehydrated at 423 K for 12 h under vacuum confirm the grafting (Figure 2). Figure 2 a shows the spectra of the bare MIL-101 compound compared with two samples after ED grafting; the ν(NH) and ν(CH) stretching regions indicate the presence of ED (the spectrum of which is also shown in the liquid phase for comparison). It is worth noting that the observed aliphatic C–H stretching vibrations (2800–3000 cm^{-1}) are shifted to larger values, as observed when the molecule is coordinated to a Lewis acid center,[15] therefore clearly demonstrating the selective ED grafting onto chromium(III) CUSs in mesoporous cages. Furthermore, as shown in Figure 2 b, the concentration of chromium(III) CUSs detected by CO adsorption at low temperature undoubtedly decreases with increasing the amount of coordinated ED. Indeed the chromium(III) CUSs completely disappear in ED-MIL-101(D), indicating full grafting of ED onto CUSs. The resulting pore modification is visible in the N_2 adsorption isotherms of the amine-grafted MIL-101. Compared with the bare MIL-101, they exhibit a significant decrease of the N_2 amount adsorbed at $P/P_0 > 0.01$ (Figure 3). The BET surface area decreases from 4230 m^{2}g^{-1} to 3555 m^{2}g^{-1} after grafting (Table 1). The pore size distribution curves (calculated by the BJH equation[16]) indicate that the amine grafting leads to a slight decrease of the pore sizes. Elemental analyses (Table 1) indicate an amine content close to one and two molecules per trimer of chromium octahedra for the ED-MIL-101 and ED-MIL-101(D) solids, respectively, which is in agreement with an effective grafting on the CUS. These results also support that the residual terephthalic species coordinated to CUSs in MIL-101 after outgassing are replaced by amine moieties during the grafting process. The grafted amine groups are assumed to be present mainly at the center of mesopore cages, leading to a slight decrease of the pore sizes, as terminal water molecules to produce chrom-

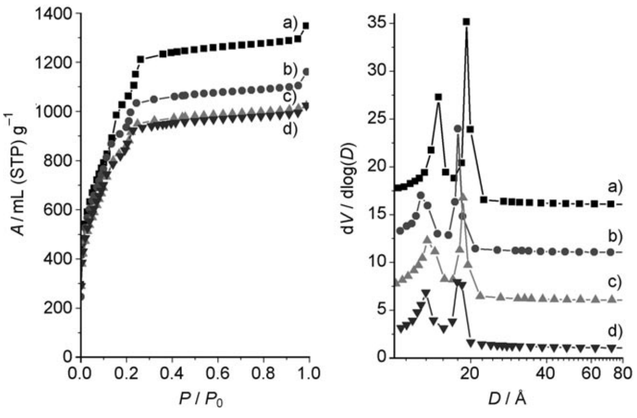
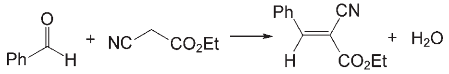


Figure 3. Nitrogen adsorption isotherms 77 K (left) and pore-size distribution curves with adsorption volume *V* and pore diameter *D* (right) of the as-synthesized and amine-grafted MIL-101. Sample a) is the as-synthesized MIL-101, and samples b)–d) are ED-MIL-101, APS-MIL-101, and DETA-MIL-101, respectively.

Table 1: Catalytic properties of the amine-grafted MIL-101 and mesoporous silica SBA-15 in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate.[a]



Catalyst	S_{BET} [$m^2 g^{-1}$][b]	N content [mmol g^{-1} cat.][c]	Conv. [%]	Sel [%][d]	TOF [h^{-1}]
MIL-101	4230	–	31.5[g]	99.4[g]	–
ED-MIL-101	3555	2.07 (1.04)[f]	97.7[g]	99.1[g]	328
ED-MIL-101(D)[e]	3257	3.96 (1.98)[f]	97.7[h]	99.3[h]	214
DETA-MIL-101	3215	3.03 (2.02)[f]	97.7[g]	99.3[g]	190
APS-MIL-101	3306	1.14	96.3[g]	99.3[g]	168
SBA-15	780	–	2.6[g]	93.0[g]	–
APS-SBA-15	510	2.89	74.8[i]	93.5[i]	32

[a] Reaction was carried out with 1 mmol of benzaldehyde, 1 mmol of ethylcyanoacetate, and 20 mg of catalyst in 25 mL of cyclohexane at 353 K. [b] S_{BET}: BET surface areas obtained from N_2 adsorption isotherms. [c] Determined by elemental and thermogravimetric analyses. [d] Sel: selectivity for *trans*-ethyl cyanocinnamate. [e] ED-MIL-101(D): ED-grafted MIL-101 obtained by two times higher ED concentration than that in ED-MIL-101. [f] Numbers in parentheses denote the content of free amine group(s) available for the reaction. [g] The reaction time was 19 h. [h] 7 h, and [i] 16 h. [j] TOF (turnover frequency): Moles of product formed per mole of nitrogen in the grafted MIL-101 or the APS-SBA-15 per hour.

ium(III) CUSs are directed towards the center of the cages. The thermal stability of the grafted amine groups is also an important issue for further applications. Indeed, infrared spectra recorded after outgassing of ED-MIL-101 with increasing temperatures confirm the thermal stability of amine species at least up to 473 K, as shown in the Supporting Information, Figure S3.

The catalytic performance of dehydrated ED-MIL-101 in base catalysis were measured by using the Knoevenagel condensation as a base-catalyzed model reaction[4a] and its activities compared to those of the APS-grafted mesoporous silica SBA-15 (APS-SBA-15). Table 1 shows the catalytic results of the condensation of benzaldehyde with cyanoethyl acetate over various amine-grafted molecular sieves at 353 K. The dehydrated mesoporous silica SBA-15 has only negligible activity, whereas the dehydrated MIL-101 revealed low but distinctive catalytic activity (31.5 % conversion at 19 h). The origin of activity in MIL-101 should be further clarified in future work. Interestingly, for a small amount of catalyst (20 mg, or 1.12 M), catalytic activities of ED-MIL-101 are noticeably better than those of APS-SBA-15, even though the content of free amine groups in ED-MIL-101 (1.04 mmol g^{-1}) is significantly lower than that of APS-SBA-15 (2.89 mmol g^{-1}). However, the activity of ED-MIL-101(D) is not much larger than that of ED-MIL-101, which is probably due to the different reactivities of grafted amine species (Table 1, and see the Supporting Information, Figure S4). For the condensation of benzaldehyde into *trans*-ethyl cyanocinnamate, the conversion for ED-MIL-101 is 97.1 %, with high selectivity (99.1 %). By contrast, APS-SBA-15 exhibits only 74.8 % conversion, with 93.5 % selectivity. Moreover, in terms of turnover frequency (TOF), ED-MIL-101 shows a remarkably superior activity (10 times higher than that of APS-SBA-15). In this case, TOF values of the grafted MIL-101 were calculated after subtracting the catalytic activity of MIL-101 from those of the grafted MIL-101. The higher activity of ED-MIL-101 might be mainly attributed both to the easily accessible amine functional groups and to its high surface area. The lower activity of APS-SBA-15 can be ascribed to the actual loss of catalytically active sites by the formation of H-bonds between functional groups.[17] The recyclability test of ED-MIL-101 clearly supports that it is easily isolated from the reaction suspension by filtration and can be reused without significant loss of activity in the third run (see the Supporting Information, Figure S5).

Remarkably, ED-MIL-101 reveals the size dependence on catalytic activities owing to the change of the substituent groups of carbonyl compounds in the Knoevenagel condensation. For example, with benzophenone, the condensation reaction with malonitrile is hard to realize (see the Supporting Information, Figure S6) because the formation of the quite large product, 1,1-dicyano-2,2-diphenylethene, might be occluded in the pores, indicating the transition state or product shape-selectivity already known in microporous zeolites.[18] The size-selective reactivity in ED-MIL-101 points out that the reaction essentially takes place in the amine-grafted pores taking into consideration the guest-selective properties of a 3D-porous coordination polymer with amide groups in the base-catalyzed Knoevenagel condensation.[13b] This led us to tune the pore size of MIL-101 by the type and shape of grafting agents leading to the pore modification.

The current successful concept of amine grafting onto CUSs has a very important consequence: the encapsulation of metals, for which only few attempts have been made until now.[6a,19] For example, Fischer and co-workers have performed the loading of metals, such as palladium and copper, onto MOF host lattices by the adsorption of metal organic CVD precursors.[19a] Although the range of observed nanoparticle sizes are above the dimensions of the cage, the corresponding solids exhibited distinct catalytic properties. Paik Suh and co-workers have tried to generate nanoparticles of silver and gold in situ within a flexible nickel-containing MOF by the reduction of noble metals by the Ni^{2+} center of a cyclam complex.[19b] The nickel-containing MOF network was intact, whereas the generated nanoparticles were not incorporated between the layers. Therefore, inclusion of metallic nanoparticles in MOFs still remains a challenge. In this work, we propose another important way for the encapsulation of noble metals, such as palladium, platinum, and gold over the amine-grafted MIL-101 according to the procedure depicted in Figure 1E. The encapsulation procedure (see the Supporting Information) comprises the neutralization of the surface amine groups with an aqueous HCl solution, ionic reactions of the positively charged surface ammonium groups with anionic noble metal salts, that is, $[PdCl_4]^{2-}$, $[PtCl_6]^{2-}$, and $[AuCl_4]^{-}$, by anionic exchange of the chloride anions, and finally the gentle reduction of noble metals with $NaBH_4$ at low temperature. After the encapsulation of noble metals, there is no apparent loss of crystallinity in X-ray diffraction patterns, and no supplementary Bragg peaks appear, but the intensities of those peaks of MIL-101 change specifically for each metal, confirming their introduction into the pores (see the Supporting Information, Figure S7). TEM images of 1 wt% noble-metal-containing MIL-101 materials (0.93–0.96 wt% based on inductively coupled plasma analysis) also support the successful encapsulation with the detection of fine nanoparticles in the range of 2–4 nm, in agreement with the cage diameters, although some of nanoparticles still remain outside the pores (see the Supporting Information, Figure S8). The formation of much larger palladium particles (>20 nm) in palladium-impregnated MIL-101 further verifies the superior effect of amine-grafting to encapsulation of noble metals (Supporting Information, Figure S8e). Moreover, palladium-loaded APS-MIL-101 and ED-MIL-101 have obviously high activities (Figure 4) during the Heck reaction at 393 K, which is the most powerful method to couple alkenes with organic moieties.[20] Herein, the coupling reaction of acrylic acid with iodobenzene was concerned. Their activities were comparable with that of a commercial Pd/C catalyst (1.09 wt% Pd) after a certain induction period (0.5–1 h), probably owing to the slow diffusion of reactants to reach accessible metal sites in the pores. The recyclability test of palladium-loaded MIL-101 (not shown) confirms that the reaction takes place mainly in a heterogeneous manner. The extension of the present strategy will open up the development of versatile hybrid materials with new functions.

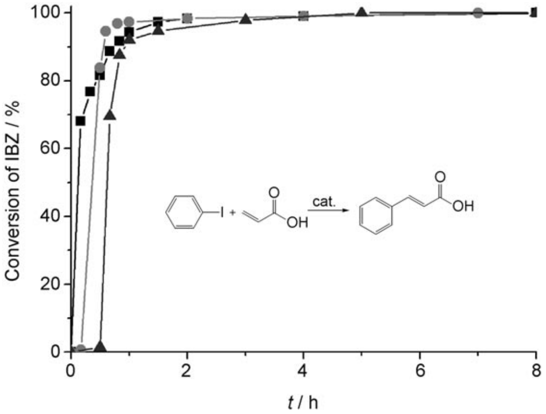


Figure 4. Catalytic activities of various palladium-loaded catalysts as a function of reaction time *t* in the Heck coupling reaction. Symbols: ■ Pd/C (1.09 wt% Pd); ● Pd/APS-MIL-101 (0.93 wt% Pd); ▲ Pd/ED-MIL-101 (0.95 wt% Pd). Reaction was carried out with 1.0 mmol of iodobenzene (IBZ), 1.5 mmol of acrylic acid, 1.5 mmol of triethylamine and 50 mg of catalyst in 25 mL of *N*,*N*-dimethylacetamide as a solvent at 393 K.

In conclusion, the presence of chromium(III) CUSs in chromium(III) terephthalate MIL-101 with zeotypic giant pores has been found to provide an intrinsic chelating property with electron-rich functional groups, leading to the formation of the thermally stable amine species grafted in the surface. This feature offers a powerful way to selectively functionalize the unsaturated sites in MIL-101. It was demonstrated that ED and DETA can be used as new grafting agents to produce the amine-grafted MIL-101, exhibiting the remarkably high activities in the Knoevenagel condensation. The present approach ensures the development of newly functionalized materials through the immobilization of organic molecules and the encapsulation of metal components.

Experimental Section

MIL-101 was initially prepared from hydrothermal reaction of terephthalic acid with $Cr(NO_3)_3\cdot 9H_2O$, HF, and H_2O at 493 K for 8 h. The as-synthesized MIL-101 was further purified by a three-step process using double filtration, hot ethanol, and aqueous NH_4F solutions (see the Supporting Information). ED-MIL-101, DETA-MIL-101, and APS-MIL-101 were prepared as follows: In a typical procedure, MIL-101 (0.5 g), dehydrated at 423 K for 12 h, was suspended in anhydrous toluene (30 mL). To this suspension, 0.75 mmol of ED, DETA, and APS were added separately, and the mixture was stirred with heating to reflux for 12 h. For ED-MIL-101(D), 1.5 mmol of ED was used, but the other reaction conditions were the same. APS-SBA-15 was prepared by using calcined mesoporous silica SBA-15 ($S_{BET} = 780\,m^2g^{-1}$, $V_{pore} = 1.16\,mL\,g^{-1}$) according to a similar procedure reported in the literature.[21] Detailed methods for characterization are described in the Supporting Information.

All catalytic measurements for the Knoevenagel condensation and Heck reaction were carried out in a glass flask (50 mL) equipped with a reflux condenser and a magnetic stirrer. Before the reaction, the amine-functionalized materials and the palladium-encapsulated materials were treated at 423 K for 12 h under vacuum to remove residual water in the samples. The products were analyzed using a gas chromatograph (Donam DS6200) equipped with a capillary column (DB-WAX) and a flame ionization detector. Detailed methods for catalytic measurements and analysis are described in the Supporting Information.

Received: December 31, 2007
Revised: February 19, 2008

Keywords: grafting · heterogeneous catalysis · metal–organic frameworks · surface functionalization · unsaturated metal sites

---

[1] *Handbook of porous solids* (Eds.: F. Schüth, K. S. W. Sing, J. Weitkamp), Wiley-VCH, Weinheim, **2002**.

[2] See, for example: a) A. Vimont, J.-M. Goupil, J.-C. Lavalley, M. Daturi, S. Surblé, C. Serre, F. Millange, G. Férey, N. Audebrand, *J. Am. Chem. Soc.* **2006**, *128*, 3218; b) M. Dinca, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 11172; c) S. S.-Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Prpen, I. D. Williams, *Science* **1999**, *283*, 1148; d) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 2186; e) P. M. Forster, J. Eckert, B. D. Heiken, J. B. Parise, J. W. Yoon, S. H. Jhung, J.-S. Chang, A. K. Cheetham, *J. Am. Chem. Soc.* **2006**, *128*, 16846; f) P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Férey, A. K. Cheetham, *J. Am. Chem. Soc.* **2003**, *125*, 1309.

[3] a) A. Vimont, H. Leclerc, F. Maugé, J. C. Lavalley, M. Daturi, S. Surblé, C. Serre, G. Férey, *J. Phys. Chem. C.* **2007**, *111*, 383; b) L. Alaerts, C. E. A. Kirschhock, M. Maes, M. A. van der Veen, V. Finsy, A. Depla, J. A. Martens, G. V. Baron, P. A. Jacobs, J. F. M. Denayer, D. E. De Vos, *Angew. Chem.* **2007**, *119*, 4371; *Angew. Chem. Int. Ed.* **2007**, *46*, 4293.

[4] See, for example: a) X. Wang, Y. Tseng, J. C. C. Chan, S. Cheng, *J. Catal.* **2005**, *233*, 266; b) S. Huh, H.-T. Chen, J. W. Wiench, M.

Pruski, V. S.-Y. Lin, *Angew. Chem.* **2005**, *117*, 1860; *Angew. Chem. Int. Ed.* **2005**, *44*, 1826.

[5] a) A. P. Wight, M. E. Davis, *Chem. Rev.* **2002**, *102*, 3589, and references therein; b) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem.* **2006**, *118*, 3290; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216.

[6] a) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191, and references therein; b) H. Li, M. Eddaoudi, M. O'Keefe, O. M. Yaghi, *Nature* **1999**, *402*, 276; c) A. K. Cheetham, C. N. R. Rao, R. K. Feller, *Chem. Commun.* **2006**, 4780; d) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466.

[7] See for example: a) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238; b) D. G. Samsonenko, H. Kim, Y. Sun, G.-H. Kim, H.-S. Lee, *Chem. Asian J.* **2007**, *2*, 484; c) X. Zhao, B. Xiao, A. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012; d) M. Latroche, S. Surblé, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J.-H. Lee, J.-S. Chang, S. H. Jhung, G. Férey, *Angew. Chem.* **2006**, *118*, 8407; *Angew. Chem. Int. Ed.* **2006**, *45*, 8227; e) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670; f) M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, J. R. Long, *J. Am. Chem. Soc.* **2006**, *129*, 11175; g) A. G. Wong-Foy, A. J. Matzger, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 3494.

[8] See, for example: a) J. W. Yoon, S. H. Jhung, Y. K. Hwang, S. M. Humphrey, P. T. Wood, J.-S. Chang, *Adv. Mater.* **2007**, *19*, 1830; b) P. L. Llewellyn, S. Bourrelly, C. Serre, Y. Filinchuk, G. Ferey, *Angew. Chem.* **2006**, *118*, 7915; *Angew. Chem. Int. Ed.* **2006**, *45*, 7751; c) J. Won, J. S. Seo, J. H. Kim, H. S. Kim, Y. S. Kang, S.-J. Kim, Y. Kim, J. Jegal, *Adv. Mater.* **2005**, *17*, 80; d) R. Q. Snurr, J. T. Hupp, S. T. Nguyen, *AIChE J.* **2004**, *50*, 1090; e) B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi, S. Dai, *Angew. Chem.* **2006**, *118*, 1418; *Angew. Chem. Int. Ed.* **2006**, *45*, 1390.

[9] See, for example: a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982; b) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151; c) C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940; d) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563; e) P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki, G. Férey, *Chem. Commun.* **2007**, 2820; f) P. M. Forster, A. K. Cheetham, *Top. Catal.* **2003**, *24*, 79; g) L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs, D. E. De Vos, *Chem. Eur. J.* **2006**, *12*, 7353.

[10] P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, *Angew. Chem.* **2006**, *118*, 6120; *Angew. Chem. Int. Ed.* **2006**, *45*, 5974.

[11] a) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305; b) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[12] Z. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2007**, *129*, 12368.

[13] a) S. Kitagawa, S.-I. Noro, T. Nakamura, *Chem. Commun.* **2006**, 701; b) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 2607.

[14] a) G. Férey, C. Mellot-Draznieks, C, Serre, F, Millange, J, Dutour, S, Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040; b) S. H. Jhung, J.-H. Lee, J. W. Yoon, C. Serre, G. Férey, J.-S. Chang, *Adv. Mater.* **2007**, *19*, 121.

[15] a) K. Krishnan, R. A. Plane, *Inorg. Chem.* **1966**, *5*, 852; b) D. A. Young, T. B. Freedman, E. D. Lipp, L. A. Nafie, *J. Am. Chem. Soc.* **1986**, *108*, 7255.

[16] E. P. Barrett, L. G. Joyner, P. P. Halenda, *J. Am. Chem. Soc.* **1951**, *73*, 373.

[17] M. W. McKittrick, C. W. Jones, *Chem. Mater.* **2003**, *15*, 1132.

[18] M. Schenk, B. Smit, T. J. H. Vlugt, T. L. M. Maesen, *Angew. Chem.* **2001**, *113*, 758; *Angew. Chem. Int. Ed.* **2001**, *40*, 736.

[19] See, for example: a) S. Hermes, M. Schröter, 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; b) H. R. Moon, J. H. Kim, M. Paik Suh, *Angew. Chem.* **2005**, *117*, 1287; *Angew. Chem. Int. Ed.* **2005**, *44*, 1261; c) D. Zacher, A. Baunemann, S. Hermes, R. A. Fischer, *J. Mater. Chem.* **2007**, *17*, 2785.

[20] L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133.

[21] J. M. Kim, Y. Sakamoto, Y. K. Hwang, Y. U. Kwon, O. Terasaki, S.-E. Park, G. D. Stucky, *J. Phys. Chem. B* **2002**, *106*, 2552.