DOI: 10.1002/ange.200600105

Hydrogen Storage in the Giant-Pore Metal–Organic Frameworks MIL-100 and MIL-101**

Michel Latroche, Suzy Surblé, Christian Serre, Caroline Mellot-Draznieks, Philip L. Llewellyn, Jin-Ho Lee, Jong-San Chang, Sung Hwa Jhung, and Gérard Férey*

Nowadays, energetic needs are mainly covered by fossil fuels with concomitant pollutant emissions responsible for global warming. Among the possible solutions to reduce the greenhouse effect, hydrogen has been proposed for energy transportation. Indeed, this gas can be seen as a clean and efficient energy carrier. However, besides the difficulties related to hydrogen production, high-capacity storage is still to be developed. Hydrogen can be stored as a compressed gas, liquefied in tanks, and ab- or adsorbed in solids.[1–3] Many compounds are able to store large amounts of hydrogen. Such solid-state solutions are of interest in terms of safety, global yield, and long-term storage. However, to be suitable for applications, such compounds must have high capacity, good reversibility, fast reactivity, and sustainability. Two different approaches are possible for solid-state storage of hydrogen. In the first, the hydrogen molecule is dissociated and H atoms form chemical bonds with the solid (chemisorption). Such a process allows a very high volumetric density at temperatures and pressures close to ambient conditions. However, storage in metal hydrides has the drawback of low weight capacities, essentially due to the high molar mass of heavy metals such as

---

[*] Dr. M. Latroche
Laboratoire de Chimie Métallurgique des Terres Rares
CNRS, UPR 209, 94320 Thiais Cedex (France)
Fax: (+33) 149-781-203
E-mail: michel.latroche@iscsa.cnrs.fr

S. Surblé, Dr. C. Serre, Dr. C. Mellot-Draznieks, Prof. G. Férey
Institut Lavoisier
UMR 8180
Université de Versailles—St Quentin en Yvelines
45 Avenue des Etats-Unis, 78035 Versailles Cedex (France)

Dr. P. L. Llewellyn
MADIREL
UMR 6121
Université de Provence-CNRS
Centre de Saint Jérôme
13397 Marseille Cedex 20 (France)

J.-H. Lee, Dr. J.-S. Chang, Dr. S. H. Jhung
Korea Research Institute of Chemical Technology
Jang-dong 100, Yuseong-Gu, 305-600 Daejon (South Korea)

[**] The authors are grateful to Dr. A. Vimont and Pr. M. Daturi (LCS, Caen, France) for the preliminary in situ IR experiments. J.-S.C. would like to thank KRICT for supporting this work under the institutional research program.

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

lanthanides and zirconium. This can be overcome by using materials made of much lighter elements such as magnesium or vanadium, which exhibit higher capacities (7.6 wt% for Mg), but high temperatures, typically 300°C, are required to fully desorb hydrogen[1,4] and the kinetics remain too slow for practical applications. The second approach consists of physisorption of hydrogen on the surface of solids. In this case, there is no chemical dissociation, binding energies are much lower than for chemisorption, and the process has significant capacity but at low temperature, typically that of liquid nitrogen. In the past, exceptionally high storage capacities have been claimed for carbon nanostructures.[5,6] However, these results were not confirmed, and it has been demonstrated that carbon materials cannot store large amounts of hydrogen at room temperature.[7–12] Other porous materials have been investigated, for example, zeolites,[13] but their capacity remains below 1.8 wt% at 77 K. For these microporous materials, many authors have attempted to relate hydrogen capacities to specific areas at low temperature, but Nijkamp et al.[14] concluded that the relation is not straightforward and a better correlation can be found with the micropore volume. This was recently confirmed with the adsorption of hydrogen in ordered nanostructured carbons.[15]

Metal–organic frameworks (MOFs) are a new class of storage materials with low density and high specific area. They are built up by linking inorganic clusters with various organic linkers[16] through strong bonds, and some of them show very promising results for hydrogen adsorption. For example, MOF-5, with large cubic cavities, adsorbs up to 4.7 wt% under 60 bar at 77 K,[17] but the disparity of the results between the various authors[18–20] underlines the importance of careful activation of the sample for good results. We reported hydrogen sorption on the metal terephthalates MIL-53 or $M(OH)[C_6H_4(CO_2)_2]$[21] ($M = Al^{3+}$, Cr^{3+}; MIL: material from Institut Lavoisier), which exhibit one-dimensional (1D) channels with large free diameters of about 8.5 Å. Their hydrogen storage capacities are 3.2 (M = Cr) and 3.8 wt% (M = Al) when loaded at 77 K under 1.6 MPa. In the same system, two chromium carboxylates MIL-100 and MIL-101 with giant pores exist.[22,23] These hybrid solids are built up from carboxylate moieties (benzene-1,3,5-tricarboxylate (btc) for MIL-100; benzene-1,4-dicarboxylate (bdc) for MIL-101) and trimeric chromium(III) octahedral clusters which have removable terminal water molecules and therefore provide potential unsaturated metal sites in the structure. The resulting zeotype architectures (Figure 1) are built by the connection of large hybrid supertetrahedra which further assemble with formation of very large mesopores. The cell volumes are huge (ca. 380000 and ca. 702000 Å³, respectively), and the smaller of the two types of quasispherical cages are delimited by 12 pentagonal faces, and the larger ones by 16 faces (12 pentagonal and four hexagonal). After removal of the guests, the accessible diameters are 25 and 29 Å for MIL-100 and 29 and 34 Å for MIL-101. The as-prepared materials contain water and free carboxylic acid within the pores. Their evacuation prior to gas loading induces significant weight loss without any loss of crystallinity under the given thermal conditions.[24]

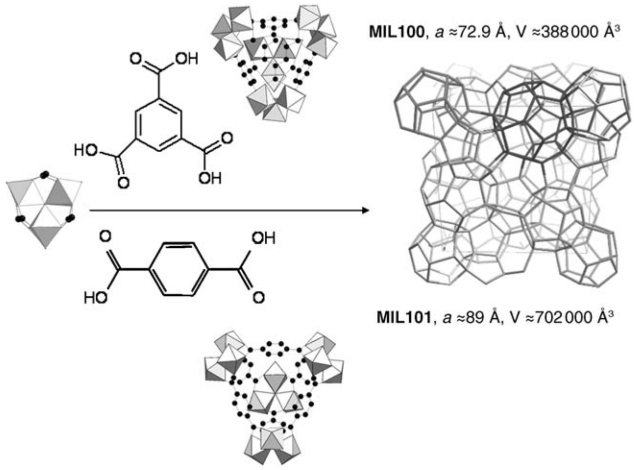

Figure 1. Schematic view of the porous solids MIL-100 and MIL-101. Left: trimers of chromium octahedra which assemble with either btc (MIL-100) or bdc (MIL-101) to form the hybrid supertetrahedra; right: the resulting zeotype architecture (each intersection of cages is occupied by a supertetrahedron).

A powdered sample of MIL-100 outgassed at 220°C overnight shows a large weight loss of 36.4%, which corresponds to expectation. The density of the outgassed sample, measured with helium gas, is 2.63 g cm^{-1}, and the Langmuir surface area is close to 2800 m^2 g^{-1}. The hydrogen uptake, measured at 298 and 77 K, shows a very fast adsorption process and thermodynamic equilibrium is reached in a few seconds, as expected for physisorption. At room temperature, the hydrogen gas isotherm curve increases linearly with pressure up to 0.15 wt% under 7.33 MPa (Figure 2). At 77 K, hydrogen adsorption is significant at low pressure, with a maximum capacity of 3.28 wt% under 2.65 MPa. Increasing the pressure to 8.5 MPa leads to a saturation plateau without further hydrogen uptake. The curve, typical of a type-I or Langmuir isotherm profile, shows good reversibility on desorption.

In the case of MIL-101, two different treatments were considered. The first treatment (MIL-101a) consisted, as for

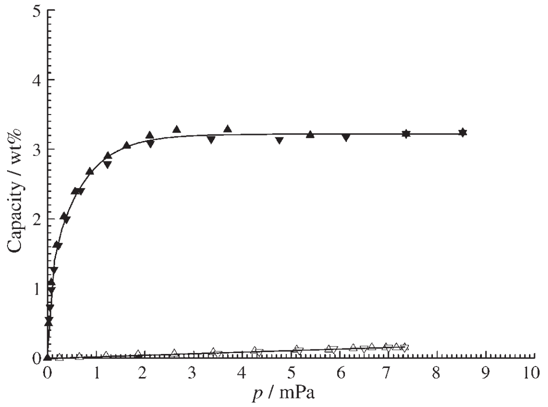

Figure 2. Adsorption (point-up triangles) and desorption (point-down triangles) pressure–composition isotherm (PCI) curves for MIL-100 at 298 (empty symbols) and 77 K (full symbols). Lines are guides to the eye.

MIL-100, of heating the as-synthesized sample, which contains traces of recrystallized bdcH$_2$ and significant amounts of bdcH$_2$ within the pores, at 220 °C under vacuum overnight. The second sample (MIL-101b) was obtained in the same synthesis conditions as the first but activated by additional treatment steps (see Supporting Information for details). In the latter case, most of the bdcH$_2$ has been evacuated. Preliminary in situ IR experiments showed that this sample contains 10–15 wt% coordinated bdcH$_2$, and therefore only half of the metal sites are poisoned by coordinated bdcH$_2$ molecules. The Langmuir surface areas were close to 4000 (MIL-101a) and 5500 m^{2}g^{-1} (MIL-101b). The densities measured after outgassing were 2.26 (a) and 1.74 g cm^{-1} (b). Hydrogen uptake was measured for both MIL-101a and MIL-101b at 298 and at 77 K. Once more, the adsorption/desorption processes are very fast.

At 298 K, MIL-101a shows a linear increase of the adsorption curve up to 0.36 wt% under 8.6 MPa (Figure 3). No saturation is observed, despite a small inflexion of the curve above 6 MPa. Measurement of the desorption branch down to 1.1 MPa shows good reversibility, and the two curves approximately coincide. At 77 K, the isotherm increases rapidly at moderate pressure to reach maximum capacity at 4.5 wt% with a saturation plateau above 4.0 MPa. The curve is reversible on desorption and shows a typical type-I or Langmuir isotherm profile (Figure 3).

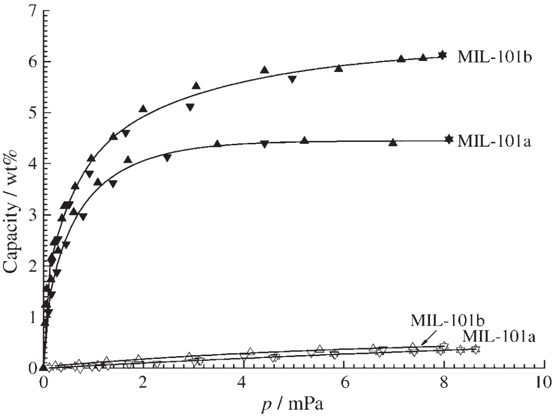

Figure 3. Adsorption (point-up triangles) and desorption (point-down triangles) pressure–composition isotherm (PCI) curves for MIL-101a and MIL-101b at 298 (empty symbols) and 77 K (full symbols). Lines are guides to the eye.

MIL-101b exhibits larger hydrogen uptake at both temperatures. Under ambient conditions, the gain in weight capacity is small (0.43 wt% under 8 MPa) but significant compared to MIL-101a under the same conditions. At 77 K, the capacity increases with pressure up to 6.1 wt% at 8 MPa, but again saturation is almost reached above 4 MPa.

The observed reversible capacities at room temperature for MIL-100 and MIL-101a,b are not negligible and slightly larger than those reported recently by Panella et al.[17] for MOF-5 and Cu$_3$(btc)$_2$ (0.28 and 0.35 wt%, respectively). However, they are relatively low compared to the values typically reported for metallic hydrides (between 2 and 3%, depending on metal composition and desorption temperature). Volumetric densities are also low at room temperature (ca. 4–8 g(H$_2$) dm^{-3}), as compared to the 150 g(H$_2$) dm^{-3} easily achievable with a compound like LaNi$_5$.

At 77 K, MIL-100 and MIL-101b show significant capacities (3.3 and 6.1 wt%, respectively) under moderate pressures. The value for MIL-100 is comparable to those reported for activated carbon and recently published MOFs,[17] while MIL-101b exhibits one of the highest values reported so far for hydrogen physisorption at this temperature (see Table 1). Moreover, preliminary IR spectroscopic experiments indicate that 10–15 wt% of the incorporated bdcH$_2$ still remains trapped in the pores of MIL-101b. Larger capacities are therefore expected if the activation process can be further improved.

For nanostructured carbons hydrogen uptake is reported to be linearly proportional to the specific surface area with a slope of about (1.5–2) × 10^{-3} wt% m^{-2}g.[9,25,26] Accordingly, the very large surface areas developed in MIL-10X structures ($X = 0$ or 1) suggest capacities should be very high. However such a relation is not straightforward. The porous chromium terephthalate MIL-53, with 1D empty channels, has a Langmuir surface area close to 1500 m^{2}g^{-1} and a reversible capacity of 3.2 wt% at 77 K under 1.6 MPa.[21] In the present studies, the Langmuir surface areas of the samples reach 2700 m^{2}g^{-1} (MIL-100) and between 4000 and 5500 m^{2}g^{-1} (MIL-101a,b), several times that of MIL-53. Despite these much larger surface areas, the capacity increase of 90% relative to MIL-53 is smaller than expected. This confirms that surface area is not the only criterion for hydrogen adsorption. Indeed, one would expect that in systems with ultramicropores, that is, pores of up to three times the size of the probe molecule, volume filling should also occur. However, the ratio between capacity uptake and Langmuir surface area is almost constant for the MIL-10X compounds, that is, such a relationship is probably valid for compounds having similar structural properties.

Clearly, the very large empty space generated by large cages is useless for gas storage. To retain hydrogen in the tunnels and cages of porous solids, one needs strong interactions between the walls and the H$_2$ molecules, provided that the pores are sufficiently large to accommodate H$_2$ molecules. This is supported by recent work by Jhung et al. on nanoporous aluminophosphates showing that small pore size and large micropore volume are beneficial for high hydrogen uptake.[27] A recent neutron-diffraction analysis at 3.5 K on deuterated MOF-5,[28] confirmed later,[29] identified its H$_2$ adsorption sites. Four positions for hydrogen molecules were reported. Two sites were found to be filled first: one at the center of the three ZnO$_3$ triangular faces and one on top of the single ZnO$_3$ triangle. On further loading, two additional adsorption sites are occupied: one above the two oxygen ions and one at the top of the hexagonal linkers. Moreover, the relative binding energies were found to be larger for the three sites around the clusters than for those around the organic linkers. This important result clearly shows that the metal oxide cluster is primarily responsible for adsorption, while the organic linker plays only a secondary role.

Table 1: Summary of hydrogen adsorption in MOFs at 77 K.

Material[a]	Free apertures[b,c] [Å]	Apparent surface area[d] [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$][g]	H_2 uptake [wt %]	Conditions	Heat of adsorption [$kJ mol^{-1}$][j–m]	Ref.
$Mn(HCO_2)_2$	3/4.7	297[f]	–	0.9	1 atm	n.a.	[33]
Ni(cyclam)(bpydc)	6.1/7.6	817	0.37	1.1	1 atm	n.a.	[34]
$Zn_2(bdc)_2(dabco)$	7.8/9.5	1450[e]	–	2.0	1 atm	n.a.	[35]
$Ni_2(bpy)_3(NO_3)_4$ (M)	2.4/4.0	–	0.181[h]	0.8	1 atm	n.a.	[36]
$Ni_2(bpy)_3(NO_3)_4$ (E)	2.1/4.2	–	0.149[h]	0.7	1 atm	n.a.	[36]
$Ni_3(btc)_2(3\text{-pic})_6(pd)_3$	8.5/10.7	–	0.63	2.1	14 bar	n.a.	[36]
$Cu_2(pzdc)_2(pyz)$, CPL-1	3.4/5.0	–	–	0.2	1 atm	n.a.	[37]
$Cu_2(bptc)$, MOF-505	6.7/8.3/10.1	1830	0.63	2.48	1 atm	n.a.	[38]
$Sc_2(bdc)_3$	≈5.3	721[e]	0.33	1.5	0.8 bar	n.a.	[39]
$M_3[Co(CN)_6]_2$ M = Mn, Fe, Co, Ni, Cu, Zn	≈2/4.5	720–870[e]	n.a.	1.4–1.8	1 bar	−5.3–7.4[j]	[40]
$Mg_3(ndc)_3$	≈3.5	190[i]	n.a.	0.48	1.17 bar	−7–9.5[j]	[32]
AOH)(bdc), MIL-53(Al)	8.4	1590	0.59	3.8	16 bar	n.a.	[21]
Cr(OH)(bdc), MIL-53(Cr)	8.5	1500	0.56	3.2	16 bar	n.a.	[21]
$Al_3O(OH)(btc)_3$, MIL-96(Al)	≈3/6	–	n.a.	1.7	10 bar	n.a.	[41]
$COF(btc)_2$, MIL-100(Cr)	25/29	2700	1.0	3.3	25 bar	−5.6–6.3[k]	this work
$Cr_3OF(bdc)_3$, MIL-101(Cr)	8.6/29/34	5500	1.9	6.1	60 bar	−9.3–10.0[k]	this work
$Cr_3OF(ntc)_{1.5}$, MIL-102(Cr)	≈4	42	0.12	0.9	10 bar	−5.99[l]	[31]
$Cu_3(btc)_2$, HKUST-1	3.5/9	1958	n.a.	3.6	50 bar	−4.5/−6.8[j]	[17,42]
$Zn_4O(bdc)_3$, MOF-5 or IRMOF-1	11.2	2296[e]	1.19	4.7	50 bar	−3.8/−4.8[j]	[17,43,42]
$Zn_4O(cbbdc)_3$, IRMOF-6	9.3	3300	1.14	4.8	50 bar	n.a.	[44]
$Zn_4O(ndc)_3$, IRMOF-8	12.6	1466	0.52	1.50	40 bar	−6.1[j]	[44,43]
$Zn_4O(hpdc)_3$, IRMOF-11	9	2340	0.68	3.5	35 bar	−9.1[j]	[44]
$Zn_4O(tmbdc)_3$, IRMOF-18	13.8	1501	0.53	0.89	40 bar	n.a.	[44]
$Zn_4O(ttdc)_3$, IRMOF-20	14	4590	1.53	6.7	70 bar	n.a.	[44]
$Zn_4O(BTB)_2$, MOF-177	11/17	5640	1.59	7.5	70 bar	n.a.	[44]
$Cu_2(bptc)$	6.5	1670[e]	0.68	4.02	20 bar	n.a.	[45]
$Cu_2(tptc)$	7.3	2247[e]	1.08	6.06	20 bar	n.a.	[45]
$Cu_2(qptc)$	8.3	2932[e]	1.14	6.07	20 bar	n.a.	[45]

[a] Abbreviations: bdc = benzene-1,4-dicarboxylate; ndc = naphthalene-2,6-dicarboxylate; hpdc = 4,5,9,10-tetrahydropyrene-2,7-dicarboxylate; tmbdc = 2,3,5,6-tetramethylbenzene-1,4-dicarboxylate; btb = benzene-1,3,5-tribenzoate, cyclam = 1,4,8,11-tetraazacyclotetradecane; bpydc = 2,2′-bipyridyl-5,5′-dicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane; bpy = 4,4′-bipyridine; btc = benzene-1,3,5-tricarboxylate; 3-pic = 3-picoline; pd = 1,2-propanediol; ttdc = thieno[3,2-*b*]thiophene-2,5-dicarboxylate; bptc = biphenyl 3,3′:5,5′-tetracarboxylate; tpdc = terphenyl 3,3′′:5,5′′-tetracarboxylate; qpdc = quaterphenyl 3,3′′′:5,5′′′-tetracarboxylate. [b] Calculations were performed using the Cerius2 software package. Crystallographic data for the evacuated frameworks were used where available. [c] Free diameters correspond to the largest spheres that can pass through the apertures of the frameworks. [d] Calculated for N_2 adsorption data collected at 77 K using the Langmuir model except where indicated. [e] BET surface area from N_2 at 77 K. [f] BET surface area for CO_2 at 195 K. [g] Calculated from N_2 adsorption data collected at 77 K by using the Dubinin–Radushkevich method, except where indicated. [h] Methanol used as adsorbate. [i] Calculated from O_2 adsorption data collected at 77 K by using the BET model. [j] Values obtained by calculation (from adsorption experiments at different temperatures). [k] Value at low coverage measured directly by microcalorimetric experiments. [l] Values deduced from computer simulation. [m] n.a.: not available.

With this in mind, it is interesting to compare the results obtained with MIL-100 and MIL-101 with those of the metal benzenedicarboxylate MIL-53 or $Cr(OH)(O_2CC_6H_4CO_2)$,[21] which has a very similar composition to MIL-101. MIL-53 does not exhibit any H_2 sorption capacity at room temperature, whereas MIL-100 and MIL-101 do. The presence in MIL-100 or $Cr_3F(H_2O)_2O[C_6H_3(CO_2)_3]_2$ and MIL-101 or $Cr_3F(H_2O)_2O[C_6H_4(CO_2)_2]_3$ of fluorine atoms and of unsaturated chromium sites (i.e., after removal of the terminal water molecules) provides possible sites for strong interaction which may explain the present hydrogen-storage properties observed at 300 K. To understand more deeply the differences in hydrogen adsorption of these large-pore samples, microcalorimetric experiments were performed at 77 K and low pressures (< 1 bar) on both samples with dihydrogen as the gas. Surprisingly, the enthalpy of adsorption in MIL-101b at low coverage is much higher, close to $-10\ kJ mol^{-1}$ (range: -9.3 to $-10.0\ kJ mol^{-1}$), than that of MIL-100 of around $-6\ kJ mol^{-1}$ (range: -5.6 to $-6.3\ kJ mol^{-1}$). According to Bathia et al.,[30] the thermodynamic requirement for an adsorbent capable of storing hydrogen at ambient temperature is a heat of adsorption of hydrogen of $15.1\ kJ mol^{-1}$. The heats of adsorption reported to date for MOFs are usually in the range 4–7 $kJ mol^{-1}$ [17,31] with the highest value of 7.0–9.5 $kJ mol^{-1}$ reported for Mg-based MOFs.[32] What could be the nature of the interaction between hydrogen molecules and the framework that gives rise to such high values for MIL-101, the highest so far reported for MOFs? Looking carefully at the structures, there could be two possibilities. First, after dehydration both mesosolids have unsaturated metal sites (i.e., five-coordinate chromium sites). However, IR experiments showed that the strongest Lewis metal sites are poisoned in MIL-101 by coordinated bdcH$_2$ moieties, whereas this is not in the case for MIL-100. This observation rules out the possibility of the unsaturated metal sites being the strongest interaction sites for hydrogen in MIL-101. The second possibility might be the presence of strong adsorption sites within the microporous supertetrahedra (ST). If their internal diameters are close to 6.6 and 8.6 Å, respectively, benzene rings of btc moieties in MIL-100 lie at the faces of the STs and leave almost no space for gas molecules to enter the cavities of the STs. On the contrary, in MIL-101, the bdc moieties lie at the edges and leave the STs open to H$_2$ molecules. Therefore, in our opinion, the most probable hypothesis is that the microporous STs of MIL-101 are the sites of strongest interaction in MIL-101, probably at each corner close to the trimers of chromium octahedra.

In conclusion, the two chromium carboxylates MIL-100 and MIL-101 adsorb large amounts of hydrogen at 77 K, with a capacity close to 6.1 wt% for MIL-101 as well as the highest heat of adsorption reported so far (10 kJ mol^{-1}) at low pressure, but relatively low hydrogen uptakes at room temperature. It seems that the small pores in MIL101 play a major role. Indeed the very large empty space generated by large cages leads to very large pores that are not as effective for H$_2$ storage as small pores. Such criteria must be taken into account in the design of new hybrid solids showing improved hydrogen-storage properties.

Received: January 10, 2006
Revised: September 22, 2006

Keywords: carboxylate ligands · chromium · hydrogen · mesoporous materials · physisorption

---

[1] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353–358.
[2] L. Schlapbach, *MRS Bull.* **2002**, 675–676.
[3] A. Züttel, *Mater. Today* **2003**, *September*, 24–33.
[4] G. Sandrock, *J. Alloys Compd.* **1999**, *293–295*, 877–888.
[5] P. Chen, X. Wu, J. Lin, K. L. Tan, *Science* **1998**, *285*, 91–93.
[6] A. Chambers, C. Park, R. T. K. Baker, N. M. Rodriguez, *J. Phys. Chem. B* **1998**, *102*, 4253–4256.
[7] M. Hirscher, M. Becher, *J. Nanosci. Nanotechnol.* **2003**, *3*, 3–17.
[8] M. Hirscher, M. Becher, M. Haluska, A. Quintel, V. Skakalova, Y.-M. Choi, U. Dettlaff-Weglikowska, S. Roth, I. Stepanek, P. Bernier, *J. Alloys Compd.* **2002**, *330–332*, 654–658.
[9] M. Hirscher, M. Becher, M. Haluska, F. von Zeppelin, X. Chen, U. Dettlaff-Weglikowska, S. Roth, *J. Alloys Compd.* **2003**, *356–357*, 433–437.
[10] M. Ritschel, M. Uhlemann, O. Gutfleisch, A. Leonhardt, A. Graff, C. Täschner, J. Fink, *Appl. Phys. Lett.* **2002**, *80*, 2985.
[11] G. G. Tibbets, G. P. Meisner, C. H. Olk, *Carbon* **2001**, *39*, 2291.
[12] S. K. Bhatia, A. L. Myers, *Langmuir* **2006**, *22*, 1688–1700.
[13] H. W. Langmi, A. Walton, M. M. Al-Mamouri, S. R. Johnson, D. Book, J. D. Speight, P. P. Edwards, I. Gameson, P. A. Anderson, I. R. Harris, *J. Alloys Compd.* **2003**, *356–357*, 710–715.
[14] M. G. Nijkamp, J. E. M. J. Raaymakers, A. J. van Dillen, K. P. de Jong, *Appl. Phys. A* **2001**, *72*, 612–623.
[15] R. Gadiou, S.-E. Saadallah, T. Piquero, P. David, J. Parmentier, C. Vix-Guterl, *Microporous Mesoporous Mater.* **2005**, *79*, 121–128.
[16] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoui, J. Kim, *Nature* **2003**, *423*, 705.
[17] B. Panella, M. Hirscher, H. Pütter, U. Müller, *Adv. Funct. Mater.* **2006**, *16*, 520–524.
[18] N. L. Rosi, J. Eckert, M. Eddaoui, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127–1129.
[19] J. L. C. Rowsell, A. R. Millward, K. S. Park, O. M. Yaghi, *J. Am. Chem. Soc.* **2004**, *126*, 5666–5667.
[20] B. Panella, M. Hirscher, *Adv. Mater.* **2005**, *17*, 538–540.
[21] G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guegan, *Chem. Commun.* **2003**, *24*, 2976–2977.
[22] G. Férey, C. Serre, F. Millange, C. Mellot-Draznieks, S. Surblé, J. Dutour, I. Margiolaki, *Angew. Chem.* **2004**, *116*, 6456; *Angew. Chem. Int. Ed.* **2004**, *43*, 6296.
[23] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040.
[24] 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*, 3218–3227.
[25] M. Becher, M. Haluska, M. Hirscher, A. Quintel, V. Skakalova, U. Dettlaff-Weglikovska, X. Chen, M. Hulman, Y. Choi, S. Roth, *C. R. Phys.* **2003**, *4*, 1055–1062.
[26] B. Panella, M. Hirscher, S. Roth, *Carbon* **2005**, *43*, 2209–2214.
[27] S. H. Jhung, H.-K. Kim, J. W. Yoon, J.-S. Chang, *J. Phys. Chem. B* **2006**, *110*, 9371.
[28] T. Yildirim, M. R. Hartman, *Phys. Rev. Lett.* **2005**, *95*, 215504.
[29] E. C. Spencer, J. A. K. Howard, G. McIntyre, J. L. C. Rowsell, O. M. Yaghi, *Chem. Commun.* **2006**, 278.
[30] S. K. Bathia, A. L. Myers, *Langmuir* **2006**, *22*, 1688.
[31] S. Surblé, C. Serre, F. Millange, T. Düren, M. Latroche, G. Férey, *J. Am. Chem. Soc.* DOI: 10.1021/ja064343u.
[32] M. Dinca, J. R. Long, *J. Am. Chem. Soc.* **2005**, *127*, 9376.
[33] D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 32–33.
[34] E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858–2861; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798–2801.
[35] D. N. Dybtsev, H. Chun, D. Kim, *Angew. Chem.* **2004**, *116*, 5143–5146; *Angew. Chem. Int. Ed.* **2004**, *43*, 5033–5036.
[36] X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinky, *Science* **2004**, *306*, 1012.
[37] Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kabo, T. C. Kobayashi, *Angew. Chem.* **2005**, *117*, 942; *Angew. Chem. Int. Ed.* **2005**, *44*, 920.
[38] B. Chen, N. W. Ockwig, A. R. Millard, D. S. Contreras, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4823; *Angew. Chem. Int. Ed.* **2005**, *44*, 4745.
[39] J. Perles, M. Iglesias, M.-A. Martin-Luengo, M. A. Monse, C. Ruiz-Valero, N. Snejko, *Chem. Mater.* **2005**, *17*, 5837–5842.
[40] S. S. Kaye, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 6506.
[41] T. Loiseau, L. Lecroq, C. Volkringer, J. Marrot, G. Férey, M. Haouas, F. Taulelle, S. Bourrelly, P. L. Llewellyn, M. Latroche, *J. Am. Chem. Soc.* **2006**, *128*, 10223.
[42] J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304.
[43] A. Dailly, J. J. Vajo, C. C. Ahn, *J. Phys. Chem. B* **2006**, *110*, 1099.
[44] A. G. Wong-Foy, A. J. Matzger, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 3494.
[45] X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey, M. Schröder, *Angew. Chem.*, **2006**, *118*, 7518–7524; *Angew. Chem. Int. Ed.*, **2006**, *45*, 7358–7364.