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Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties

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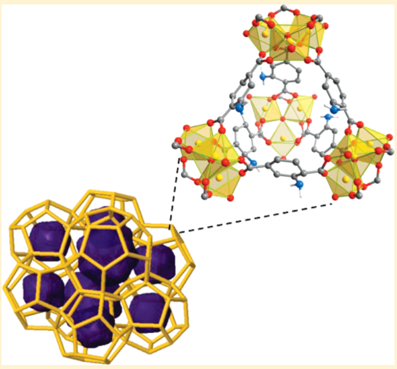
ABSTRACT: A new MIL-101 material based on aluminum and containing amine functional groups has been synthesized. The pure phase NH_2-MIL-101(Al) can only be formed in very specific synthesis conditions, where both the metal source and the solvent used play a key role. The resulting porous solid shows a high thermal and chemical stability, decomposing at temperatures above 650 K in air. The NH_2-MIL-101(Al) framework offers an excellent trade off for separation of CO_2: the combination of high stability, acceptable capacity at low adsorbate partial pressures, high selectivity, and fast regenerability makes this new material a very attractive candidate for applications like natural gas or biogas upgrading. CO_2 capacities up to 62 wt % are obtained at room temperature and 3 MPa. In addition to an excellent separation performance, the NH_2-MIL-101(Al) shows a high activity in the basic catalyzed Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate at 313 K even in an as apolar a solvent as toluene (turn over frequency, TOF = 1.8 h^{-1}).



KEYWORDS: metal organic framework, MIL-101(Al), amine, catalysis, CO_2 separation, Knoevenagel condensation

1. INTRODUCTION

Metal Organic Frameworks (MOFs) are nowadays at the front of materials research. In recent years, the combination of organic and inorganic subunits in fully crystalline porous materials has given rise to thousands of MOF structures with a vast topological richness.[1,2]

Impressive progress has been made during the past decade, yielding promising results in among others the fields of catalysis[3,4] and separation.[5,6] However, in spite of the initial enthusiasm, several factors are hampering further developments of MOF applications in these important areas of research. First, the continuous runaway status of MOF chemistry is a strong driving force for proof of principle publishing, usually leading to incomplete works that are hardly followed up. Furthermore, although several series of MOFs like MIL-101,[7] MIL-53,[8] most ZIFs,[9] CPO-27,[10] and UIO-66[11] have shown unusual thermal and chemical stability, the use of MOFs in applications like catalysis or separation is still largely limited by the lack of functional and selective sites in most ultrastable MOF frameworks. Practical routes to create functional solids include direct synthesis or post-synthetic functionalization,[12] grafting of active groups on the open metal sites of certain structures,[13] and encapsulation of active species.[14] One of the current challenges is the development of stable MOFs including functional organic sites[15] that could be used either directly or after post-synthetical modification. Indeed, most of the examples existing in the literature on post-synthetic functionalization have been performed on MOFs with a limited stability. However, the incorporation of ligands including additional functional moieties is not trivial, since such groups may directly coordinate to the metal ions, depending upon the chosen reaction conditions. For instance, only a few amine-functionalized frameworks[16−20] are known out of the more than 10000 MOF structures reported in the literature.

This work focuses on the incorporation of amine moieties in the MIL-101 framework.[21] This hybrid solid is built up from supertetrahedral (ST) building units, which are formed by rigid terephthalate ligands and trimeric metal(III) octahedral clusters (see Scheme 1). The resulting solid possesses two types of quasi-spherical mesoporous cages formed by 12 pentagonal and 16 faces, respectively. The so-called medium cavities are accessible through 1.2 nm pentagonal windows, while the large cavities are communicated through the same pentagonal windows and 1.6 nm hexagonal windows (see Scheme 1).

The presence of coordinatively unsaturated metal sites (CUS) in MIL-101 allows its use as a mild Lewis acid[22] and, more important, allows its postfunctionalization via grafting of active species.[21] The zeotype cavities of two different sizes (extended MTN topology), the fully accessible porosity, together with a high thermal and chemical stability make MIL-101 an excellent candidate for separation and catalytic purposes.

When it comes to reticular design, only MIL-101(Cr) and NH_2-MIL-101(Fe)[18] are known to date, while for other MOFs composed by trivalent metals and terephthalate linkers, that is, MIL-53, a much wider chemical composition in terms of both metals and functional linkers is known. This is not surprising considering that MIL-101 is a kinetic product and MIL-53 is the thermodynamically favored structure when starting from similar synthesis compositions.[18] This also followed from the synthesis of other amine functionalized Al MOFs, where also mixtures with

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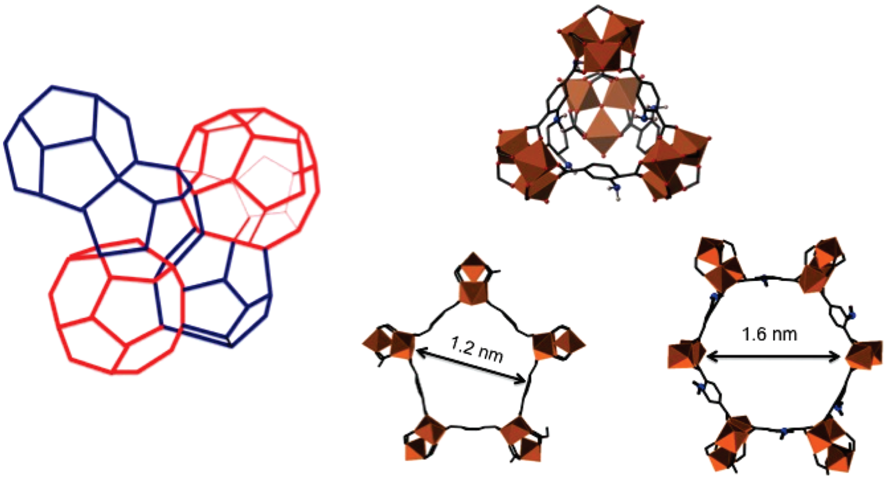
Scheme 1. Representation of the NH_2-MIL-101(Al) Framework[a]



[a] Left: MTN topology including two types of mesoporous cavities. Right: Detail of the supertetrahedra (top) and the hexagonal and pentagonal windows.

the amino MIL-101(Al) were observed.[20] The amine functionalized MIL-101(Fe) has been reported and applied in drug delivery[23] and medical imaging,[24] where the relatively low thermal and chemical stability shown by this framework does not seem to affect its outstanding performance. However, when thinking of other types of applications, the development of materials with a similar topology and stability as MIL-101(Cr) but presenting functional organic sites is needed.

Here we report the reproducible synthesis of a pure phase amine functionalized MIL-101(Al). The resulting material shows a high chemical and thermal stability. The separation properties have been assessed in terms of single component adsorption and mixture separation, demonstrating that the amine functionalized framework is an excellent candidate for the selective separation of CO_2 from methane and nitrogen. Moreover, owing to the presence of amines, the NH_2-MIL-101(Al) displays outstanding basic catalytic properties and is a perfect candidate for post-synthetic covalent functionalization.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization. *2.1.1. Synthesis.* The amino-MIL-101(Al) was synthesized by means of a solvothermal treatment involving *N*,*N*-dimethylformamide (DMF) as solvent. Starting reactants are aluminum chloride hexahydrate ($AlCl_3$ $6H_2O$, Sigma Aldrich, 99%, 0.51 g), 2-amino terephthalic acid ($HO_2C-C_6H_3NH_2-CO_2H$, Sigma Aldrich, 99%, 0.56 g) and *N*,*N*-dimethylformamide ($(CH_3)_2NCHO$, Sigma Aldrich, >99.9%, 30 mL).

The reactants were placed in a Teflon-lined autoclave and heated for 72 h at 403 K in an oven under static conditions or for 6 h at the same temperature under microwave irradiation. The resulting yellow powder was filtered under vacuum and washed with acetone.

To remove organic species trapped within the pores, the samples were activated in boiling methanol overnight and stored at 373 K.

Similar reaction conditions but using terephthalic acid as linker were tried to synthesize pure phase unfunctionalized MIL-101(Al). However, in all the attempts MIL-53(Al) was formed. On the other hand, the aluminum source used in the synthesis turned out to be crucial for the formation of the NH_2-MIL-101(Al). Similar synthesis composition using $Al(NO_3)_3$ resulted in the formation of NH_2-MIL-53(Al), as we already reported.[17,25,26]

2.1.2. Characterization Techniques. Powder X-ray Diffraction (XRD). The powder XRD experiments were carried out at the Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility. The data were collected on 0.7 mm glass capillaries filled with the sample and attached to a gas system which can reach vacuum conditions, using a MAR345 imaging plate at a sample to detector distance of 250 mm, and using a radiation with a wavelength λ = 0.709659 Å. The data were integrated using the Fit2D program and a calibration of a LaB6 standard sample. Prior to the experiments the sample was outgassed under vacuum at 473 K for 2 h. The temperature was then adjusted to 273 K, and the data were collected.

Nitrogen Adsorption. To calculate the Brunauer−Emmett−Teller (BET) surface area, nitrogen adsorption at 77 K was carried out. A Quantachrome Autosorb-6B setup was used. BET surface area is calculated over the range of relative pressures between 0.05 and 0.15. The pore volume is calculated as the uptake (cm^3/g) at a relative pressure of 0.5. The sample was pretreated before measurement, it was outgassed under vacuum at a temperature of 473 K for 16 h.

Thermogravimetrical Analysis. Thermal stability was studied using a system provided by Mettler Toledo, model TGA/SDTA851e, under an air flow of 60 mL/min at a heating rate of 5 K/min up to 873 K.

Adsorption Isotherms. High-pressure adsorption isotherms of pure CO_2 (purity of 99.995%), CH_4 (purity of 99.95%) and N_2 (purity of 99.995%) were determined using the volumetric technique with an apparatus from BEL Japan (Belsorp HP). A 0.5 g portion of amino-MIL-101(Al) sample was placed in the sample container. Before every measurement, the adsorbent was regenerated by increasing the temperature to 473 K at a rate of 10 K/min under vacuum and maintaining the temperature for 2 h.

MAS NMR. The magic angle spinning (MAS) NMR analysis was performed on a Bruker Avance-400 with a 5 mm zirconia rotor and a spinning frequency of 11 kHz. Spectra for ^{13}C and ^{27}Al were obtained.

IR Spectroscopy. Infrared (IR) spectra were recorded on KBr/NH_2-MIL-101(Al) pellets (4 wt % MOF) in a Bruker model IFS66 spectrometer in transmission mode on a high temperature/high vacuum cell with CaF_2 windows and a 633 nm laser. The spectra were collected after accumulation of 128 scans with a resolution of 4 cm^{-1}. Before collecting the spectra, the sample was pretreated in the equipment under high vacuum at 473 K for 1 h. The spectra were recorded at this temperature.

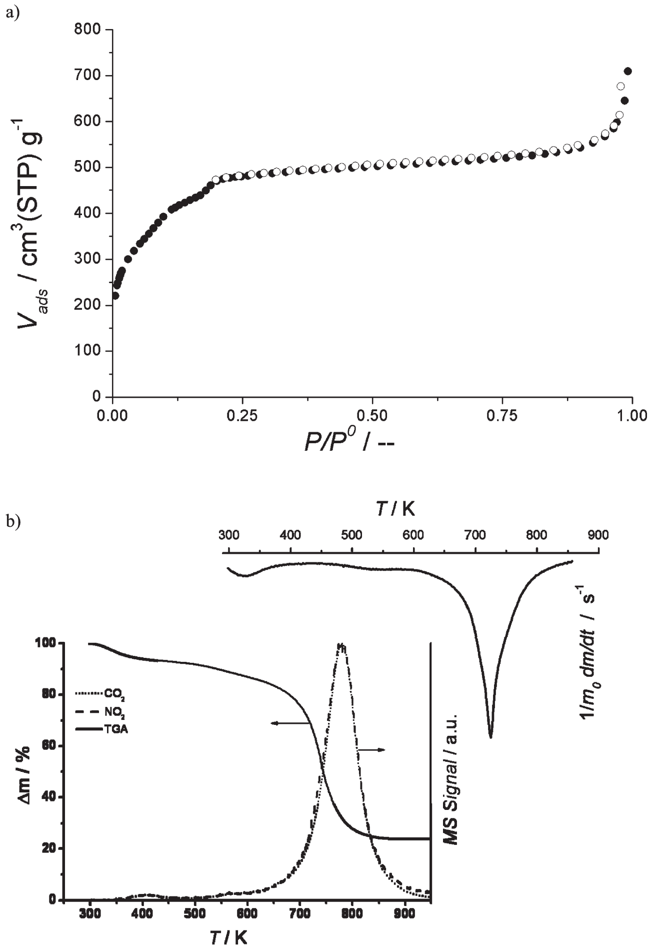


Figure 1. (a) N_2 adsorption isotherm at 77 K (closed symbols represent adsorption and open symbols the desorption loop). (b) TGA/DTG/MS analysis of the same sample in air at a heating rate of 5 K/min.

2.2. Separation Experiments. *Breakthrough Experiments.* Breakthrough experiments were carried out using a column with a length of 35 cm and an internal diameter of 1.753 mm, packed with 700 mg of pelletized (5 ton/cm^2) sample (particle size between 500 and 630 μm). More details about the experimental setup can be found elsewhere.[27,28] This system allows in situ activation of the adsorbent under a pure He flow, in this case the sample was outgassed at 473 K with a flow of helium of 6.7 mmol/min.

CO_2-CH_4 mixtures were prepared via mass flow controllers. Breakthrough experiments were carried out by step changes from He to CO_2-CH_4 flow mixtures. The dead volume of the system is calculated using hydrogen (10% of the total flow) as a reference. In the case of the NH_2-MIL-101(Al), the amount of hydrogen adsorbed at room temperature can be neglected and therefore H_2 can be used to accurately calculate the amounts of CO_2 and CH_4 adsorbed.

The gas stream at the outlet of the column was analyzed with a mass spectrometer. Since during the experiments pure gases are fed to the column, the flow rate of the gas stream at the column outlet changes from zero to the inlet flow rate throughout the adsorption process. Hence, a permanent flow of He of 6.7 mmol/min was added immediately at the outlet of the column. In this way a linear correlation between the flow rates and the measured intensities on the mass spectrometer can be assumed.

Breakthrough experiments were performed at 303 K with flow ranges from 0.36 to 0.80 mmol/min. In the figures, breakthrough curves are represented in the form of normalized molar flow rates. The adsorbed amounts, q_i and q_j, were calculated by integrating the experimental F_i versus time data. The separation factor α for a binary mixture of components i and j is calculated as follows

$$\alpha = \frac{\frac{q_i}{F_i}}{\frac{q_j}{F_j}}$$

With F_i and F_j being the molar flows of the corresponding components.

2.3. General Procedure for the Catalytic Test Reaction. *Knoevenagel Condensation.* In a typical batch experiment, an amount of the catalyst corresponding to 0.2 mmol of $-NH_2$ groups in the MOF (45.8 mg) was added to a solution of 7 mmol ethyl cyanoacetate in 5 mL of solvent in a closed Erlenmeyer flask at 313 K. After temperature stabilization, 8 mmol of benzaldehyde were added.

Instead of internal agitation, a shaking system was used to prevent attrition of the catalyst particles and to facilitate the reuse of the catalytic material. Once the reaction finished the catalyst was recovered (by filtration and centrifugation), washed with acetone and stored at 423 K.

The reaction mixture was periodically analyzed by gas chromatography using a Chrompack GC CP9001 equipped with a FID detector and a 60 m RTX-1 (1% diphenyl, 99% dimethylpolysiloxane) fused silica capillary column. Each sample was centrifuged and analyzed directly after being collected to avoid any additional conversion in the reaction mixture.

3. EXPERIMENTAL RESULTS

3.1. Characterization of the Material. *3.1.1. Nitrogen Adsorption and Termogravimetric Analysis (TGA).* Figure 1a shows the N_2 adsorption isotherm at 77 K measured on the synthesized NH_2-MIL-101(Al). The isotherm shows the well-known characteristic steps of the MIL-101 structure. These two steps are attributed to the filling of the cavities. At very low relative pressures (P/P_0 < 0.05) only the supertetrahedra are filled. As pressure increases, the medium (P/P_0 = 0.15) and later the large cavities (P/P_0 = 0.20) are filled.[21] The main difference between the amino modified MOF and its unfunctionalized counterpart MIL-101(Cr) is found in the total pore volume (measured at P/P_0 = 0.5) while for the unfunctionalized material total pore volumes of 1100 cm^3 (STP)/g are very often reported,[14,21,29,30] for the NH_2-MIL-101(Al), this value is significantly lower (500 cm^3(STP/g), but slightly higher than for the amino functionalized MIL-101(Fe).[24] The specific BET surface area for the NH_2-MIL-101(Al) is 2100 m^2/g.

In Figure 1b, the thermogravimetric analysis (TGA/DTG) of an activated NH_2-MIL-101(Al) in air is shown together with the evolution of the main combustion and desorption products (CO_2 and NO_2) as measured by mass spectrometry. The sample releases up to 5 wt % of water followed by desorption of some DMF at 400 K. The stability of the framework is quite remarkable: it only decomposes at temperatures above 650 K, in line with the highly stable Cr unfunctionalized counterpart, that decomposes at ≈675 K under similar conditions.[14] For comparison, the amino MIL-101(Fe) decomposes already at 400 K.[18] By integration of the CO, CO_2, NO_2, and NO signals recorded during the TGA analysis, a ratio $C/N = 8$ was calculated. In addition, an activation energy of decomposition of the NH_2-MIL-101(Al) of ~310 kJ/mol has been estimated from the heating rate variation in the TGA analysis, applying Kissinger's method.[31] This gives an indication of the stability of the structure.

3.1.2. Powder-XRD. A typical XRD pattern of the NH_2-MIL-101(Al) is shown in Figure 2 together with the simulated XRD pattern for MIL-101(Cr).[7] The comparison between the experimental and the simulated XRD patterns demonstrates the formation

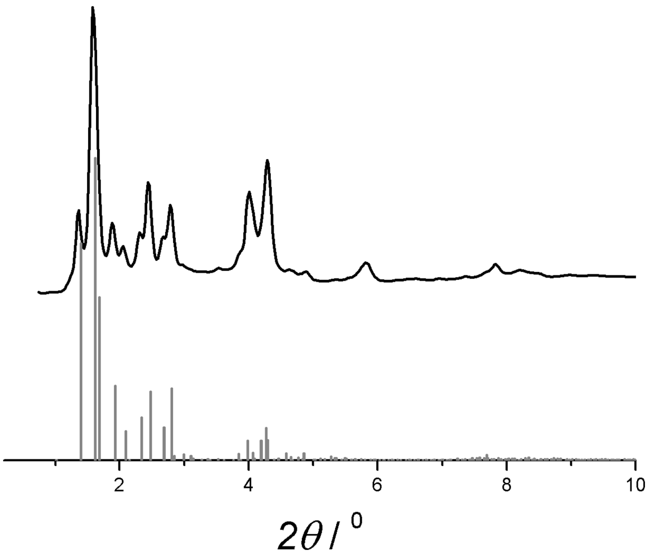


Figure 2. Power XRD for Amino-MIL-101(Al) (black) compared to that of the simulated framework for MIL-101(Cr) (gray).[7] Synchrotron radiation used with a wavelength of 0.709659 Å.

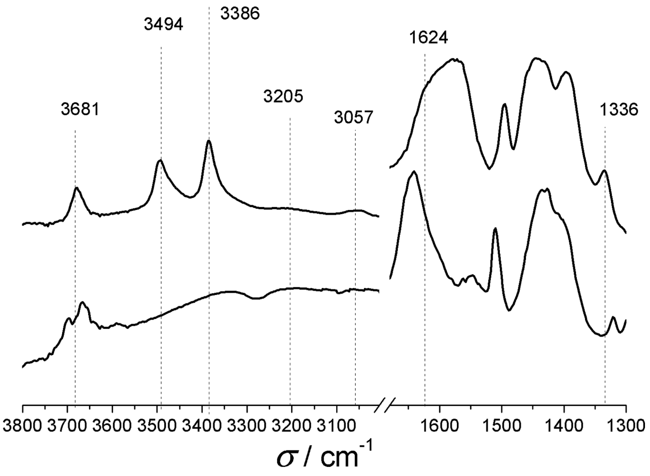


Figure 3. IR spectra (Transmittance) of Amino-MIL-101(Al) (top) compared to that of a nonfunctionalized MIL-101(Cr) (bottom).

of a pure phase NH_2-MIL-101(Al) under the applied synthesis conditions.

3.1.3. IR Spectroscopy. IR spectra were collected on activated NH_2-MIL-101(Al) samples (Figure 3). An IR spectrum of an unfunctionalized MIL-101(Cr) is shown for comparison. Focusing on the high wavenumber region, three main peaks are observed. The first one corresponds to the Al—OH groups present in the supertetrahedra (3681 cm^{-1}). This OH vibration is slightly blue-shifted with respect to the unfunctionalized MIL-101(Cr).[30] Similar shifts have been reported for isoreticular MILs like MIL-53 when changing the metal.[32] On the other hand, the absence of secondary OH bands, as the ones shown by the MIL-101(Cr), in the amino functionalized sample points at a lower hydrophilicity of this framework, in line with other amine functionalized MOFs.[33]

The doublet at 3494 and 3386 cm^{-1} corresponds to the asymmetrical and symmetrical stretchings of the amine moieties.[16,34] These absorptions seem to be formed by the contribution of two different bands, pointing at two amine species in the framework.

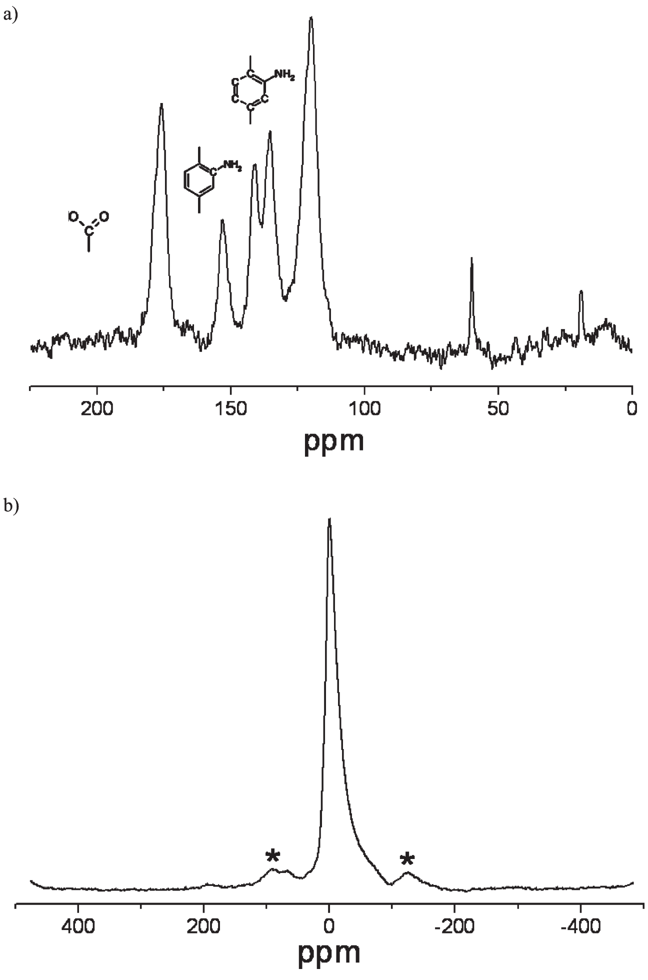


Figure 4. ^{13}C (a) and ^{27}Al NMR (b) spectra of the NH_2-MIL-101(Al).

Additionally, a new doublet appears at 3205 and 3057 cm^{-1}, suggesting the interaction of some of the amines with the framework or with each other. When focusing on the lower frequency region, in spite of the abundance of vibrations in this area, two other characteristic bands of the amino group can be perceived: the N—H bending (scissoring) vibration observed as a shoulder at 1624 cm^{-1} and the C—N stretching absorption distinctive of aromatic amines at 1336 cm^{-1}.[34]

The comparison between the peak ratios of the amine stretchings and those reported for other amino functionalized MOFs is interesting: whereas in IRMOF-3 and amino-MIL-53(Al) both stretchings have the same relative height,[16] in the case of amino-MIL-101(Al) the intensity of the symmetric peak is higher than that of the asymmetric. The much better developed amine bands in the NH_2-MIL-101(Al) IR specta compared to those reported for the NH_2-MIL-101(Fe), where the amine stretchings are hardly visible,[18] suggests a better crystallinitiy and ordering of the amines in the Al sample.

3.1.4. MAS NMR. The ^{13}C NMR spectrum of the NH_2-MIL-101(Al) (Figure 4 a) exhibits five broad chemical shifts. Four between δ = 153 and 120 ppm due to the C atoms of the phenyl ring and one signal at δ = 176 ppm caused by the carboxylic groups.[35] The two sharp signals in the high field spectrum are attributed to the presence of small residual amounts of DMF and methanol in the activated framework.

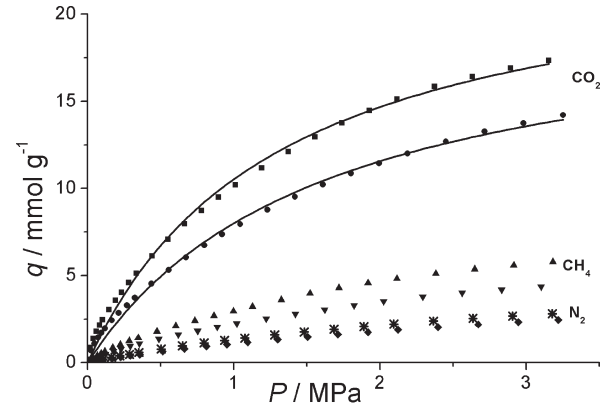


Figure 5. Adsorption isotherms for amino-MIL-101(Al). Key: ■ CO_2 at 283 K, ● CO_2 at 298 K, ▲ CH_4 at 283 K, ▼ CH_4 at 298 K, ☐ N_2 at 283 K, and ◆ N_2 at 298 K. Lines in the CO_2 isotherms correspond to a single site Langmuir fitting of the experimental data.

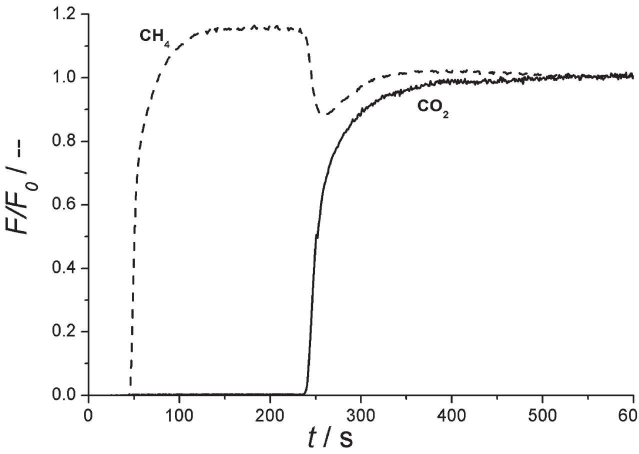


Figure 6. Breakthrough profile of CO_2 and CH_4 for a packed column of NH_2-MIL-101(Al) using a CO_2/CH_4 = 2:3 feed mixture with hydrogen at 298 K and 1 bar of total pressure. (F_{CO2} = 0.179 mmol/min; F_{CH4} = 0.2625 mmol/min; F_{H2} = 0.063 mmol/min).

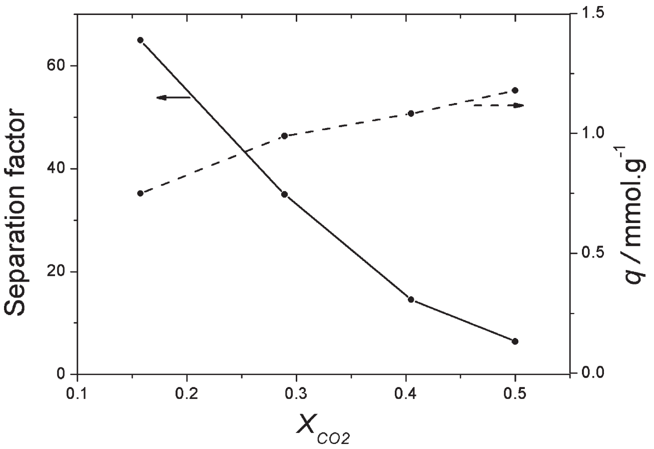


Figure 7. CO_2 adsorption capacity (full line) and CO_2/CH_4 separation factors (dashed line) at 298 K, obtained via mass balance calculations using data from breakthrough experiments at different mixture compositions. Arrows indicate the axis that should be used for each line.

The ^{27}Al NMR spectrum is shown in Figure 4b. The presence of one single signal at $\delta = 0$ ppm demonstrates that the Al in the sample has an octahedral coordination.

3.2. CO_2/CH_4 Separation. *3.2.1. High Pressure Adsorption Isotherms.* Adsorption isotherms of CO_2, CH_4, and N_2 measured at two different temperatures are shown in Figure 5. The material displays a high CO_2 capacity, while no saturation was observed in the studied range of pressures and temperatures. A large affinity for carbon dioxide over the other two gases is observed. At 298 K, the material exhibits "ideal" selectivities (ratio of the single component adsorption capacities) between 3 and 5 and between 5 and 9 for CO_2 over CH_4 and N_2, respectively, in the studied pressure range (1 to 25 bar). A single site Langmuir isotherm fit of the CO_2 adsorption data measured at different temperatures reveals a saturation uptake of CO_2 of 24.2 ± 0.2 mol/kg and an adsorption enthalpy of 22 kJ/mol.

When comparing the adsorption results with those reported for MIL-101(Cr),[30] the CO_2 capacity of the amine functionalized framework is lower (at room temperature and 3 MPa ~20 mol/kg for the Cr sample vs ~14 mol/kg for the NH_2-MIL-101(Al) sample), whereas the ideal CO_2/CH_4 selectivity is remarkably higher. In contrast, the CO_2 enthalpy of adsorption calculated for the amine functionalized MIL-101(Al) is fairly similar to that determined using calorimetry for the unfunctionalized MIL-101(Cr) (28 kJ/mol).[30]

3.2.2. Breakthrough Experiments. To assess the separation performance of the new material, gas mixture adsorption was measured from breakthrough experiments on a column packed with NH_2-MIL-101(Al). The sample was first pelletized to avoid a high pressure drop over the column. As in the case of the NH_2-MIL-53(Al), no binder was needed.[17,25,26] Figure 6 shows the breakthrough curve for the separation of a 2:3 mixture of CO_2/CH_4 at a total pressure of 1 bar and at 298 K.

A clear difference in breakthrough time between CO_2 and CH_4 was observed. During the first period both components are fully adsorbed, after that, pure CH_4 elutes from the column. The CH_4 flow rate at the outlet of the column exceeds the inlet flow rate because of a stronger adsorption for the CO_2 molecules that displaces part of the adsorbed CH_4 molecules, resulting in the so-called roll-up effect. When CO_2 starts to elute from the column, the concentration of both components at the outlet evolves to the feed concentration level, indicating that the column is saturated.

The preferential adsorption of CO_2 over CH_4 results in separation selectivities much higher than the ideal selectivities from single component adsorption. Figure 7 shows the evolution in the separation factor and the total amount adsorbed when varying the inlet composition in different breakthrough experiments at 1 bar and 298 K. Similar experiments performed on unfunctionalized MIL-101(Cr) resulted in lower separation factors: 7.5 and 3.6 for CO_2 partial pressures of 0.3 and 0.5 bar, respectively.

3.3. Catalytic Performance. The performance of NH_2-MIL-101(Al) as basic catalyst was tested in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate in different solvents at 313 K.[36,37] The molar ratio between amino groups in the MOF and the amount of ethyl cyanoacetate was 1/35. These conditions were chosen in accordance to our previous work using other amine modified MOFs.[16] The graph presented in Figure 8 shows the yield of ethyl(E)-α-cyanocinnamate, product of the condensation, based on the ethyl cyanoacetate conversion as a function of time. In both cases the selectivity achieved was close to 100%.

1,5,7-Triazabicyclo[4.4.0]dec-5-ene was used as a homogeneous catalyst under the same conditions to benchmark the activity

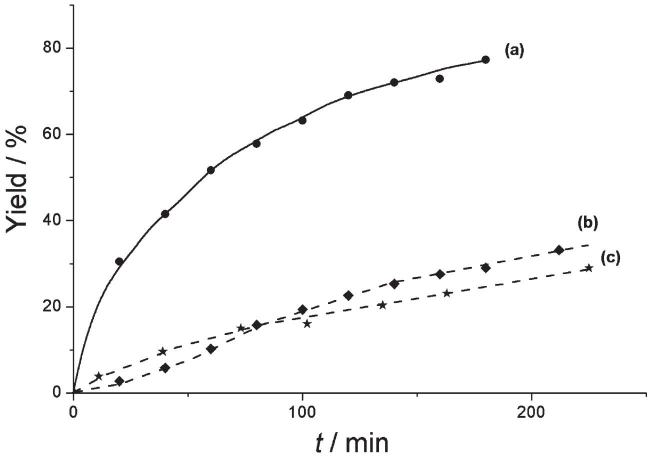


Figure 8. Knoevenagel condensation of 8 mmol of benzaldehyde and 7 mmol of ethyl cyanoacetate in 5 mL of solvent at 313 K. Yield of the product (ethyl (E)-α-cyanocinnamate) is shown as a function of time: (a) NH_2-MIL-101(Al) in DMF, (b) NH_2-MIL-101(Al) in toluene; (c) Bicycloguanidine (1,5,7-triazabicyclo[4.4.0]dec-5-ene) in toluene.

of the synthesized catalyst with a well-known strong base[38] (Figure 8). The amine modified MIL-101 shows a performance similar to that displayed by this state of the art organo-catalyst.

Apart from presenting a good catalytic activity, long-term stability and the absence of leaching are of primary importance for solid catalysts. MOF samples were reused several times to determine if the catalysts suffer from permanent deactivation. No deactivation was observed in the catalyst after several reuses.

4. DISCUSSION

A new MIL-101 material based on aluminum in the connector and containing amine functionalities has been successfully synthesized. As shown in Figure 2 a perfect match between the extended MTN topology of the targeted framework and the experimental XRD data is found.

The synthesis results demonstrate that still much work is needed to fully understand the chemistry behind MOF formation:[39,40] On the one hand, it was not possible to synthesize the unfunctionalized version of the NH_2-MIL-101(Al) when using terephthalic acid as linker. On the other hand, only syntheses using $AlCl_3$ as metal precursor in DMF as solvent resulted in the formation of the MIL-101 topology. Syntheses using $Al(NO_3)_3$ in DMF or $AlCl_3$ in H_2O delivered pure phase NH_2-MIL-53(Al). It has been widely reported that the formation of MIL-53 proceeds via MIL-101 in a complex scheme where the former is the thermodynamically favored structure and the latter the kinetically favored product. Apparently, by changing the chemical properties of the metal precursor and the solvent, kinetics might be altered resulting in the selective formation of one of the two structures.

The reason why the amine functionalized framework can be synthesized and its unfunctionalized counterpart cannot has to be related to stabilization of the framework via amine incorporation. The inclusion of amine moieties prevents to a large extent the hydrolysis of some frameworks, as clearly exemplified by the higher stability of IRMOF-3 over IRMOF-1.[12,41,42]

The NH_2-MIL-101(Al) shows a thermal stability similar to that of MIL-101(Cr), decomposing at temperatures above 650 K in an oxygen containing atmosphere.

The comparison between the available pore volume of the amine functionalized and the nonfunctionalized MIL-101 frameworks deserves special attention. The total pore volume of the amine containing the framework (Figure 1a) is half of that reported for unfunctionalized MIL-101(Cr).[7] This difference becomes even greater when taking into account differences in the framework density: aluminum is lighter than chromium. Considering that amines are not extremely bulky groups, one can think that either part of the framework is not accessible to N_2 or that a large amount of amorphous material is found together with the porous sample. The latter can be excluded in view of the good quality of the XRD and IR data, the NMR results shown in Figure 4, where the absence of free terephthalate is demonstrated, and the TGA results, where a 22% of mass (Al_2O_3) is left after framework combustion, in good agreement with an empirical framework formula of $Al_3O(DMF)[(COO)C_6H_3NH_2(COO)]_3 \cdot nH_2O$. Differences in pore volume as calculated from N_2 adsorption have then to be related to the inaccessibility of N_2 molecules to certain locations, for example, the super tetrahedra, in the framework as a consequence of the amine incorporation. In fact, the difference in CO_2 uptake, a smaller molecule (Figure 5), between the NH_2-MIL-101(Al) and the MIL-101(Cr) is much smaller (14 vs 20 mol/kg), although still considerable.

IR spectroscopy in combination with MAS NMR analysis demonstrates the integrity of the amines after inclusion in the framework. In contrast to most amine functionalized MOFs, the symmetric and asymmetric amine stretchings seem to be built up from different contributions, while an additional doublet appears at 3205 and 3057 cm^{-1}. These findings, together with the different intensity ratios of the symmetric and asymmetric stretchings, strongly suggest the presence of two different types of amine sites in the functionalized MIL-101(Al) material. We propose that this is due to the presence of amines in the supertetrahedra and in the windows (see Scheme 1). The amines present in the supertetrahedra are closer to each other and to pending −OH groups, which might result in interactions via hydrogen bonding, as we reported for the NH_2-MIL-53(Al).[43] Recently, similar differences in intensity between symmetric and asymmetric stretchings together with a secondary doublet have been reported for the NH_2-UIO-66(Zr) framework, where two different "amine sites" can be found.[34]

The benefits of amine inclusion in the framework are clear from the CO_2 separation and basic catalysis experiments. The functionalized framework shows outstanding separation properties together with fair CO_2 uptakes. The selectivity shown in the separation of mixtures is remarkably much higher than that observed for single component adsorption, which demonstrates a higher affinity for CO_2 than for CH_4 and N_2. The roll-up observed in the CO_2/CH_4 breakthrough is due to displacement of CH_4 by CO_2 and is a consequence of CO_2 depletion of the mixture along the breakthrough column and, hence, some CH_4 adsorption. These results stress the importance of mixture separation experiments. In most papers on separation properties of MOFs only single component isotherms are shown. In spite of the importance of single component adsorption, selectivity in separation can only be revealed by mixture experiments.

Another clear advantage of amine functionalized MOFs is that the presence of amines seems to help in the shaping of the particles. Structuring of porous solids from the micro- to the macro-level is essential for efficient large-scale utilization and one of the major drawbacks for many MOFs,[43,44] where the use of organic binders,[45] high temperature compaction[46] or coatings on different inert substrates are needed to achieve solid bodies. In the case of the

NH_2-MIL-101(Al) or NH_2-MIL-53(Al), only moderate pressures (5 ton/cm^2) are needed to form long-lasting pellets that can withstand hundreds of adsorption/desorption cycles. This fact has to be related to the presence of hydrogen bonding interacting species ($-NH_2$) at the surface of the particles and might have very important consequences not only for shaping, but also for the creation of, for instance, mixed-matrix type membranes.[47,48]

When the separation factor is examined as a function of the feed fraction, it is observed (Figure 7) that at low CO_2 concentrations an excellent separation is achieved on the NH_2-MIL-101(Al), while for higher CO_2 loadings, separation factors comparable to those of the state of the art sorbents for this separation are found.[49]

Much has been speculated about the extremely high adsorption capacities shown by many MOFs. However, in view of the almost linear adsorption isotherms, one must realize that, in most cases, such high capacities are only achievable at high adsorbate partial pressures. The NH_2-MIL-101(Al) is a clear example of this. Although capacities up to 14 mol/kg are measured at room temperature, corresponding to 62 wt % uptake, such CO_2 loadings are only feasible in mixtures containing high concentrations of CO_2 and in separation processes operating at high pressures, that is, in the case of many natural gas sources that cannot be used because of a high CO_2 content. In contrast, the application of such material in the capture of CO_2 from the atmosphere would never be an option. Apart from that, MOFs like the NH_2-MIL-101(Al) offer an excellent trade off between affinity and capacity: this type of linear isotherms combined with a large CO_2 affinity is perfect when also regeneration of the column is taken into account. Indeed, the studied adsorbent, showing a fair loading at low CO_2 partial pressures, can be regenerated at room temperature in a few minutes by flushing the adsorbent column with an inert gas. This combination of high stability, acceptable capacity, high selectivity, and fast and easy regeneration makes the NH_2-MIL-101(Al) an attractive candidate for applications like natural gas and biogas upgrading.

When it comes to interpret the effect of the amines on the separation performance, we recently demonstrated that the enhanced CO_2 affinity is not due to direct chemical interaction between the amines and CO_2 but to the interplay of several other factors. In the case of the amine functionalized MIL-53(Al), amines play a key role in modulating the framework flexibility, inducing shape selectivity.[43] In addition, the electrostatic properties of the framework were changed in such a way that van der Waals interactions between adsorbate and adsorbent dominate the whole adsorption process[25] In view of the nearly absent difference in CO_2 adsorption enthalpy with MIL-101(Cr), we speculate the same indirect role of the amine groups in the NH_2-MIL-101(Al).

Last but not least, the presence of free amine moieties in the framework offers interesting possibilities for catalysis and postfunctionalization. The performance of the NH_2-MIL-101(Al) in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate is better than that shown by other amino modified MOFs.[16] Even in apolar solvents the new MIL material shows an activity comparable to that of a much stronger base like 1,5,7-triazabicyclo[4.4.0]dec-5-ene[38] (Figure 8), while the catalyst can be reused without losing activity. Turnover frequencies, TOFs, at 313 K based on the total number of amine moieties of 15.4 and 1.8 h^{-1} are calculated in the presence of DMF and toluene as solvent, respectively.

The character of the solvent used in Knoevenagel condensations may have a strong effect on the reaction rate.[14,16,37,50] The polarity of the solvent affects the transition state and the capacity of the catalyst for proton transfer: when polar reagents are involved, the transition-state complex is better solvated by the solvent and the partition of the reactants at the solid−liquid interface is higher, decreasing the activation energy and enhancing the reaction rate. Moreover, some protic solvents such as ethanol may also enhance the activation of the slightly acidic benzaldehyde, yielding a higher catalytic activity. In a previous publication, we demonstrated that amino modified MOFs can be used as efficient catalysts for this interesting C−C coupling reaction. Compared to aniline, which in principle should yield a similar behavior as MOFs based on amino-terephthalic acid, the incorporation of such moiety in the open IRMOF-3 framework increased the activity of the amino group significantly. However, in a nearly apolar solvent like toluene the catalytic performance of this MOF was greatly suppressed, in clear contrast with results reported for other solid supported basic catalysts.[16] In the case of the NH_2-MIL-101(Al), however, while similar TOFs as those calculated for IRMOF-3 are found in polar (DMF) solvents, reactions in apolar (toluene) solvents results in much higher turnovers for the NH_2-MIL-101(Al). The differences found between IRMOF-3 and NH_2-MIL-101(Al) cannot be attributed to differences in diffusion rate, since both frameworks present similar pore openings, but must be due to differences in the strength of the amine moieties. Possibly the amines of the supertetrahedra might show a higher basicity than those at the windows of the NH_2-MIL-101(Al), because of specific NH_2-H_2N and NH_2-OH hydrogen bonding interactions. If true, these differences in basicity have interesting consequences not only for catalysis but also for postfunctionalization, since, in principle, it should be possible to selectively decorate certain areas of the framework (the supertetrahedra). Current work is focused on the postfunctionalization of this new material and the performance in catalysis and separation.

5. CONCLUSIONS

A new MIL-101 material based on aluminum and containing amine functionalities has been successfully synthesized. The NH_2-MIL-101(Al) shows a thermal stability similar to that of MIL-101(Cr), decomposing at temperatures above 650 K in air.

Pure phase NH_2-MIL-101(Al) can be formed under very specific synthesis conditions, where both the metal source and the solvent used play a key role.

Two different types of amine moieties are observed by IR spectroscopy, attributed to the presence of amines in the supertetrahedra and in the windows, where amines present at the supertetrahedra are in closer proximity to each other and to OH pending groups, resulting in hydrogen bonding interactions.

The NH_2-MIL-101(Al) framework offers an excellent trade off for CO_2-CH_4 separation purposes: the combination of high stability, acceptable capacity, high selectivity, and fast regenerability makes the NH_2-MIL-101(Al) a very attractive candidate for applications like natural gas and biogas upgrading.

In addition to an excellent separation performance, this new material shows a high activity in the basic catalyzed Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate even when an apolar solvent like toluene is used.

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REFERENCES

(1) Ferey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.

(2) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213.

(3) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502.

(4) Corma, A.; Garcia, H.; Xamena, F. X. L. *Chem. Rev.* **2010**, *110*, 4606.

(5) Li, J. R.; Kuppler, R. J.; Zhou, H. C. *Chem. Soc. Rev.* **2009**, *38*, 1477.

(6) Gucuyener, C.; van den Bergh, J.; Gascon, J.; Kapteijn, F. *J. Am. Chem. Soc.* **2010**, *132*, 17704.

(7) Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *309*, 2040.

(8) Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louer, D.; Ferey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519.

(9) Park, K. S.; Ni, Z.; P., A.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci.* **2006**, *103*, 10186.

(10) Dietzel, P. D. C.; Johnsen, R. E.; Blom, R.; Fjellvag, H. *Chem.—Eur. J.* **2008**, *14*, 2389.

(11) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850.

(12) Wang, Z. Q.; Cohen, S. M. *Chem. Soc. Rev.* **2009**, *38*, 1315.

(13) Hwang, Y. K.; Hong, D. Y.; Chang, J. S.; Jhung, S. H.; Seo, Y. K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Ferey, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 4144.

(14) Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Lafont, U.; Gascon, J.; Kapteijn, F. *J. Catal.* **2010**, *269*, 229.

(15) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607.

(16) Gascon, J.; Aktay, U.; Hernandez-Alonso, M. D.; van Klink, G. P. M.; Kapteijn, F. *J. Catal.* **2009**, *261*, 75.

(17) Couck, S.; Denayer, J. F. M.; Baron, G. V.; Remy, T.; Gascon, J.; Kapteijn, F. *J. Am. Chem. Soc.* **2009**, *131*, 6326.

(18) Bauer, S.; Serre, C.; Devic, T.; Horcajada, P.; Marrot, J.; Ferey, G.; Stock, N. *Inorg. Chem.* **2008**, *47*, 7568.

(19) Savonnet, M.; Bazer-Bachi, D.; Bats, N.; Perez-Pellitero, J.; Jeanneau, E.; Lecocq, V.; Pinel, C.; Farrusseng, D. *J. Am. Chem. Soc.* **2010**, *132*, 4518.

(20) Ahnfeldt, T.; Guillou, N.; Gunzelmann, D.; Margiolaki, I.; Loiseau, T.; Ferey, G.; Senker, J.; Stock, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 5163.

(21) Hong, D.-Y.; Hwang, Y. K.; Serre, C.; Ferey, G.; Chang, J.-S. *Adv. Funct. Mater.* **2009**, *19*, 1537.

(22) Henschel, A.; Gedrich, K.; Kraehnert, R.; Kaskel, S. *Chem. Commun.* **2008**, 4192.

(23) Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette, P.; Kreuz, C.; Chang, J. S.; Hwang, Y. K.; Marsaud, V.; Bories, P. N.; Cynober, L.; Gil, S.; Ferey, G.; Couvreur, P.; Gref, R. *Nat. Mater.* **2010**, *9*, 172.

(24) Taylor-Pashow, K. M. L.; Della Rocca, J.; Xie, Z. G.; Tran, S.; Lin, W. B. *J. Am. Chem. Soc.* **2009**, *131*, 14261.

(25) Couck, S.; Remy, T.; Baron, G. V.; Gascon, J.; Kapteijn, F.; Denayer, J. F. M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9413.

(26) Boutin, A.; Couck, S.; Coudert, F.-X.; Serra-Crespo, P.; Gascon, J.; Kapteijn, F.; Fuchs, A. H.; Denayer, J. F. M. *Microporous Mesoporous Mater.* **2011**, *140*, 108.

(27) van Miltenburg, A.; Gascon, J.; Zhu, W.; Kapteijn, F.; Moulijn, J. A. *Adsorption* **2008**, *14*, 309.

(28) Gascon, J.; Blom, W.; van Miltenburg, A.; Ferreira, A.; Berger, R.; Kapteijn, F. *Microporous Mesoporous Mater.* **2008**, *115*, 585.

(29) Chowdhury, P.; Bikkina, C.; Gumma, S. *J. Phys. Chem. C* **2009**, *113*, 6616.

(30) Llewellyn, P. L.; Bourrelly, S.; Serre, C.; Vimont, A.; Daturi, M.; Hamon, L.; De Weireld, G.; Chang, J. S.; Hong, D. Y.; Hwang, Y. K.; Jhung, S. H.; Ferey, G. *Langmuir* **2008**, *24*, 7245.

(31) Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.

(32) Volkringer, C.; Loiseau, T.; Guillou, N.; Ferey, G.; Elkaim, E.; Vimont, A. *Dalton Trans.* **2009**, 2241.

(33) Tagliabue, M.; Farrusseng, D.; Valencia, S.; Aguado, S.; Ravon, U.; Rizzo, C.; Corma, A.; Mirodatos, C. *Chem. Eng. J.* **2009**, *155*, 553.

(34) Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S. r.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. *Chem. Mater.* **2010**, *22*, 6632.

(35) Ahnfeldt, T.; Gunzelmann, D.; Loiseau, T.; Hirsemann, D.; Senker, J.; Férey, G.; Stock, N. *Inorg. Chem.* **2009**, *48*, 3057.

(36) Climent, M. J.; Corma, A.; Dominguez, I.; Iborra, S.; Sabater, M. J.; Sastre, G. *J. Catal.* **2007**, *246*, 136.

(37) Rodriguez, I.; Sastre, G.; Corma, A.; Iborra, S. *J. Catal.* **1999**, *183*, 14.

(38) Rao, Y. V. S.; De Vos, D. E.; Jacobs, P. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2661.

(39) Surble, S.; Millange, F.; Serre, C.; Ferey, G.; Walton, R. I. *Chem. Commun.* **2006**, 1518.

(40) Millange, F.; Medina, M.; Guillou, N.; Ferey, G.; Golden, K. M.; Walton, R. I. *Angew. Chem., Int. Ed.* **2010**, *49*, 763.

(41) Ingleson, M. J.; Barrio, J. P.; Guilbaud, J.-B.; Khimyak, Y. Z.; Rosseinsky, M. J. *Chem. Commun.* **2008**, 2680.

(42) Zhang, X.; Llabres i Xamena, F. X.; Corma, A. *J. Catal.* **2009**, *265*, 155.

(43) Stavitski, E.; Pidko, E. A.; Couck, S.; Remy, T.; Hensen, E. J. M.; Weckhuysen, B. M.; Denayer, J.; Gascon, J.; Kapteijn, F. *Langmuir* **2011**, *27*, 3970.

(44) Ramos-Fernandez, E. V.; Garcia-Domingos, M.; Juan-Alcañiz, J.; Gascon, J.; Kapteijn, F. *Appl. Catal., A* **2011**, *391*, 261.

(45) Finsy, V.; Ma, L.; Alaerts, L.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. *Microporous Mesoporous Mater.* **2009**, *120*, 221.

(46) Küsgens, P.; Zgaverdea, A.; Fritz, H.-G.; Siegle, S.; Kaskel, S. *J. Am. Ceram. Soc.* **2010**, *93*, 2476.

(47) Bae, T.-H.; Lee, J. S.; Qiu, W.; Koros, W. J.; Jones, C. W.; Nair, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 9863.

(48) Gascon, J.; Kapteijn, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1530.

(49) D'Alessandro, D. M.; Smit, B.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058.

(50) Corma, A.; Iborra, S.; Rodriguez, I.; Sanchez, F. *J. Catal.* **2002**, *211*, 208.