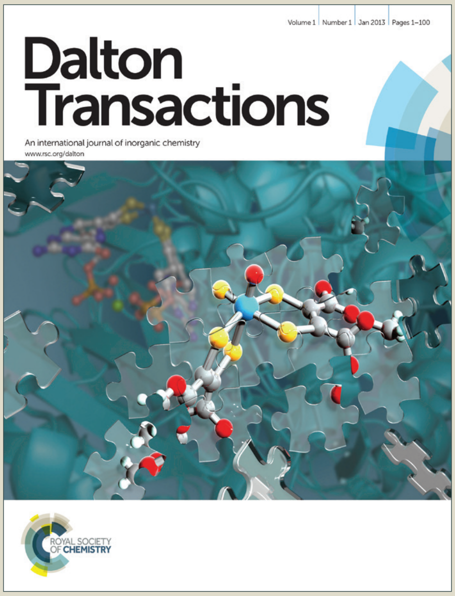
Dalton Transactions

Accepted Manuscript



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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

High-yield, fluoride-free and large-scale synthesis of MIL-101(Cr)†

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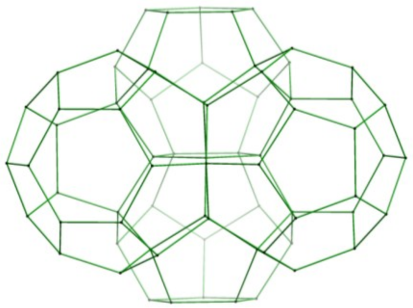
Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

MIL-101(Cr), one of most important prototypical MOFs, is well investigated and widely used in many scientific fields. With regard to MOF synthesis in general, the addition of a modifier is commonly used to improve the properties of the products. The effect of inorganic (mineral) and organic acid modifiers was thoroughly investigated in the synthesis of MIL-101(Cr) and HNO_3 could increase the yield to over 80% of a product with average $S_{BET} > 3200$ m^2/g in repeated experiments (from an average of 50% in most published syntheses) in small-scale laboratory synthesis. The large-scale synthesis could use the finding of HNO_3 addition and produce MIL-101(Cr) in >100 g quantities with yields near 70% and BET-surface areas near 4000 m^2/g. The addition of acetic acid (CH_3COOH) together with seeding could decrease the reaction temperature, lowest being 160 °C (from typically 220 °C in published procedures), with still relatively good yield and BET surface area of the product. The use of other strong inorganic or weak carboxylic acids as modulators typically caused decrease in yield and porosity.

Introduction

Metal-organic frameworks (MOFs) receive continuous attention[1,2] due to their high porosity which promises applications in, *e.g.*, gas storage,[3,4] gas[5,6,7] and liquid[8] separation processes, drug delivery,[9] heterogeneous catalysis,[10] heat transformation[11,12,13] etc.[14]

MIL-101(Cr)[15] is a three-dimensional chromium terephthalate-based porous material with the empirical formula $[Cr_3(O)X(bdc)_3(H_2O)_2]$ (bdc = benzene-1,4-dicarboxylate, X = OH or F). Its structure resembles the augmented MTN zeolite topology. MIL-101(Cr) has two types of inner cages with diameters of 29 Å and 34 Å, and pore aperture windows diameter of up to 16 Å (Fig. 1, Fig.S1 in ESI†) with high surface area (BET surface area of 4000 m^2/g).[15] MIL-101(Cr) has terminal water molecules connected to the octahedral trimeric Cr(III) building units, which can be removed under high vacuum, thus, creating potential Lewis acid sites.[16,17] MIL-101(Cr)[12] and its ligand-modified derivatives[18,19] show remarkable stability towards water, which makes it most suitable for applications in the presence of moisture/water.[12,18,19]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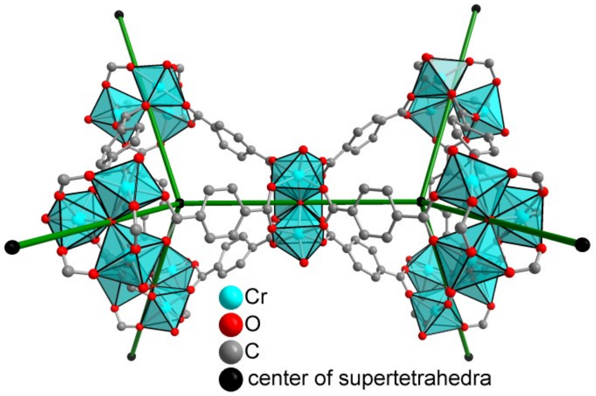

(b)

Fig. 1 (a) Zeolite-type framework presentation of the MIL-101 structure by showing the topological connectivity (in green) of the centers of the vertex-sharing supertetrahedra (b), with the $\{Cr_3(\mu_3\text{-}O)X(H_2O)_2\}$ (X = OH or F) secondary builiding unit at the vertices of a tetrahedron. Thereby, two types of mesoporous cages (a) with pentagonal and hexagonal windows are formed. The smaller cage with only pentagonal windows has a van-der-Waals pore diameter of 2.9 nm, the larger cage with pentagonal and hexagonal windows of 3.4 nm. For further presentations of the pore and window size see Fig. S1 in ESI†. Building blocks for MIL-101, $[Cr_3(\mu_3\text{-}O)X(bdc)_3(H_2O)_2]$, generated from the deposited X-ray data file at the Cambridge Structure Database (CSD-Refcode OCUNAK)[15] using the program DIAMOND.[20]

MIL-101(Cr) has evolved into one of the most important prototypical MOFs. MIL-101(Cr) or its derivatives are used as catalysts, e.g., in the oxidation of aryl sulfide to corresponding sulfoxide,[21] epoxidation of alkenes[22,23] in presence of H_2O_2, cyanosilylation of aldehydes,[24] desulfurization of dibenzothiophene.[25] Amine-grafted MIL-101(Cr) has been used as catalyst for Knoevenagel condensation reaction with high yield and high selectivity.[16] Pd loaded on amine-grafted MIL-101(Cr) was applied as a catalyst for the Heck reaction;[26] it showed high activity and strong durability in visible-light induced photocatalytic H_2 production.[27] Similarly Cu nanoparticles embedded in MIL-101(Cr) were high performance catalysts for the reduction of aromatic nitro compounds.[28] Fe_3O_4 nanoparticles embedded in MIL-101(Cr) behaved as a magnetic nanocatalyst for the solvent free oxidation of benzyl alcohol in the presence of TBHP.[29] $CoAl_2O_4$ nanoparticles embedded in MIL-101(Cr) have proved to be efficient catalysts for oxidative catalysis.[30] Recently MIL-101(Cr) and its phospho-tungstic acid (PTA) composite material have been studied as heterogeneous acid catalyst in the acetalization of aldehydes with alcohols.[31] Functionalized MIL-101(Cr) has been investigated for heterogeneous catalysis in the condensation reaction of aldehydes with alcohols.[32]

MIL-101 (Cr) with pyridine adsorbed has been used for the high-performance liquid chromatographic separation of tocopherols.[33] The adsorption properties of MIL-101(Cr) towards 1,2-dichloroethane (DCE), ethyl acetate (EA), and benzene in the presence of water vapour was investigated. The order of affinity was found to be DCE > EA > benzene.[34]

MIL-101(Cr) in polysulfone (PSF) mixed-matrix membranes (MMMs) exhibited a remarkable four-fold increase in the permeability of O_2 and CO_2 compared to pure PSF for possible O_2/N_2, CO_2/N_2 or CO_2/CH_4 gas separations. MIL-MMMs for O_2/N_2 separation had a constant selectivity of 5–6,[35] for CO_2 over N_2 or CH_4 the selectivity increases from about 20 to 25 with increasing MIL wt%.[36] MIL-101(Cr) loads of up to 24% were achieved in PSF, and the MIL-101(Cr) particles showed excellent adhesion with polysulfone in the mixed-matrix membranes and remarkable long term stability.

Post-synthetic modification (PSM) of the benzene-1,4-dicarboxylate ligand in MIL-101(Cr) using nitrating acid (HNO_3/H_2SO_4) can influence, for example, the water uptake behaviour.[37] PSM can create or modify suitable functionality in the organic linkers in preformed MOFs.[38,39] Nitro and amino functional groups were introduced in MIL-101(Cr) under extremely strong acidic condition (nitrating acid for nitration and $SnCl_2$/conc. HCl for reduction to $–NH_2$).[35] Moreover, partially functionalized materials with two different organic ligands in the same framework have been synthesized, which are difficult to obtain through direct synthesis.[18] Mixed-linker MIL-101(Cr) was recently synthesized with bdc derivatives containing $-NH_2$, $-NO_2$, -H, $-SO_3H$, -Br, -OH, $-CH_3$, and -COOH.[19]

The unique combination of properties highlighted above, such as outstanding hydrolytic stability, large surface area and pore sizes, low price of synthetic precursors, presence of functional metal sites and various possibilities for postsynthetic modification makes MIL-101(Cr) an excellent candidate for industrial applications.

Syntheses of MIL-101(Cr)

The initial MIL-101(Cr) synthesis reports a fluorine-free route but also the addition of an equimolar amount of hydrofluoric acid (HF) to chromium and H_2bdc. The obtained products are isostructural.[15] Accordingly, MIL-101(Cr) is given the empirical sum formula $[Cr_3(O)X(bdc)_3(H_2O)_2]$ (X = OH or F) where either F^- or OH^- and two aqua ligands occupy the terminal positions in the three Cr octahedra which form the trinuclear $\{Cr_3(\mu_3\text{-}O)X(H_2O)_2\}$ secondary building unit (Fig. S1 in ESI†). Small scale syntheses involve the use of HF, as a so-called mineralizing agent, which ensure unsurpassed crystallinity and a BET surface area up to 4200 m^2/g.[15,17] Several small-scale synthesis procedures are reported in the literature (see Table 1). Most follow the original synthesis procedure by Férey *et al.*[15] In this original procedure HF was used and a yield of only ~50% was stated after separation of MIL-101 from the terephthalic acid. A yield of ~50% for MIL-101 is not very satisfying in view of the lengthy synthesis and necessary separation from unused terephthalic acid. Also, the use of dangerous HF is not desirable for large-scale syntheses. HF is classified as a chemical toxicant; it is a highly corrosive liquid, and also a contact poison. Because of the ability of hydrofluoric acid to penetrate tissue, life-threatening poisoning can occur readily through exposure of skin or eyes, and more readily when inhaled or even swallowed. HF must therefore be handled with extreme care, using protective equipment and safety precautions beyond those used with other mineral acids.[40] Apart from HF, researchers also tried to use other additives in the small scale syntheses of MIL-101(Cr). For instances, using NaOH instead of HF to get nano-sized (50 nm) MIL-101(Cr) has been reported, and the product possesses relatively good BET surface area (~3200 m^2/g) and fairly good yield (37%).[41] The particle size of MIL-101(Cr) can be controlled from 19(4) nm to 84(12) nm, by using a monocarboxylic acid as a mediator, with the BET surface area reaching 2900 m^2/g.[42] Weakly alkaline lithium/potassium acetate was employed to assist the synthesis of high-quality MIL-101(Cr) (BET surface area up to 3400 m^2/g).[43] Hydrofluoric acid and sodium acetate were used as mineralizing agents to obtain hierarchically mesostructured MIL-101(Cr).[44] Evidently, the influence of pH is not clear as both acidic or basic conditions are possible

The concomitant drawbacks are the toxicity of hydrofluoric acid, relatively low reported yield at approximately 50%[15] and questionable reproducibility, as there is a large spread of surface area values, with most of them in the interval of 2400-3500 m^2/g (Table 1). The reported work-up procedures are tedious and could include size-selective / double filtrations for separation of larger crystals of terephthalic acid and prolonged washings, including such environmentally non-benign agents as NH_4F.[16] In order to obtain pure MIL-101(Cr) materials, the as-synthesized MIL-101(Cr) needs to be purified by washing processes using hot water (70 °C, 5 h), hot ethanol (60 °C, 3 h), hot aqueous NH_4F solutions (60 °C, 10 h) and rinsing with hot water at least 5 times to remove fluoride and other starting material residues.[16,17] Thus, the use of fluoride and the necessary washing procedures are mayor obstacles for large-scale manufacturing. Indeed, MIL-101 type of compounds are not represented among the Basolite® series of MOFs produced by BASF and commercialized by Aldrich, despite recognized importance[45] and the interest towards its production that was announced as early as in 2009.[46]

Stimulated by this background we screened a number of acidic modulators·[47] in the synthesis of MIL-101 and compared them with fluoride-assisted syntheses under simplified work-up conditions. We report an optimization study which resulted in the development of a high-yield procedure with proven scalability.

Table 1 Summary of surface areas of reported MIL-101(Cr).[a]

Additive	Time (h)	Temperature (°C)	Yield (%)[b]	S_{BET} (m²/g)	V_{pore} (cm³/g)	Ref.
HF	8	220	~50	~4100	2.02	15
HF	8	220	n.a. [b]	2231	1.08	48
HF	8	220	n.a. [b]	2233	1.20	49
HF	8	220	n.a. [b]	2651	1.29	50
HF	8	220	n.a. [b]	2846	1.30	51
HF	8	220	~47	2931	1.45	52
HF	8	220	n.a. [b]	2995	1.31	53
HF	8	220	~53	3007	1.51	54
HF	8	220	~50	3200	2.10	55
NaOH	24	210	~37	~3200	1.57	41
none	18	218	~64 [d]	~3460	not given	56
HF	8	220	n.a. [b]	~3020	1.80	26
HF	8	220	~57	~2367	1.46	24
HF	8	220	n.a. [b]	~2693	1.30	57
HF	8	220	n.a. [b]	~2220	1.13	58
HF	8	220	n.a. [b]	~3115	1.58	59
HF	8	220	n.a. [b]	~2059	1.10	12
TMAOH[c]	24	180	~88 [e]	~3197	1.73	60
TMAOH[c]	24	180	~50	~3060	1.45	61,62
TMAOH[c]	24	180	~47	~3055	1.51	32
HF	8	220	n.a. [b]	~3318	2.02	63
HF	8	220	n.a. [b]	~2800	1.47	18

[a] The preparation followed the original hydrothermal synthesis procedure by Férey *et al.*[15].

[b] The yield is based on Cr and refers to the isolated material after the washing procedures. When no yields were given (n.a.) and the original procedure by Férey *et al.*[15] was followed a yield of ~50% can be assumed. We note that significant water uptake of ~1 g(H_2O)/g(MIL) can occur at 40-50% room humidity which will lead to higher weights than the truly empty material.

[c] TMAOH = tetramethylammonium hydroxide.

[d] This is a singular high-yield synthesis differing from all other reports.

[e] This value is singular and perhaps doubtful; the repeated syntheses in our group (Ref. 32, 61, 62) only gave a yield of about 50%.

Results and discussion

By trying to replace HF as an acid additive we tested various inorganic and organic acids under otherwise identical conditions. During these experiments, two acid additives became noteworthy, nitric acid and acetic acid. Thereby we found that HNO_3 led to a reproducible increase in yield to over 80% with BET surface areas around and over 3200 m²/g. On the other hand the use of acetic acid in MIL-101(Cr) synthesis allowed to significantly decreasing the reaction temperature. A significant amount of terephthalic acid can still be present inside the pores and mixed with the MIL crystallites. The residual reactants and eventually the solvent needed to be removed from the pores in order to obtain a material as porous as possible. All synthesis products underwent the same purification, that is, washing and drying (activation) procedure. The products synthesized in this work are typically synthesized without HF, thus, the formulae of MIL-101(Cr) frameworks from this work do not contain F atoms and should be $[Cr_3(O)(OH)(bdc)_3(H_2O)_2]$.

High-yield, small-scale synthesis

According to literature, a typical synthesis of MIL-101(Cr) lasts 8 h at ~220 °C (Table 1). Additives are commonly used in the synthesis; especially HF which can act as a mineralizing agent to increase the crystallinity of microporous materials and favors the formation of highly crystalline phases in MOFs.[64]

We tried to replace the modifier/additive HF by other mineral and also by organic acids, including both strong mineral and weak carboxylic acid with varying coordination capabilities of the corresponding anions. Acidic modulators received less attention compared to basic ones, due to the perception that acidification should shift the equilibrium away from the formation of MIL-101(Cr) as nitric acid is released during the process. When the addition of HNO_3 showed promising results, HNO_3 synthesis experiments with varying amounts were conducted to reveal the optimal synthetic conditions. The reaction was carried out with addition of 0.25, 0.5, 0.75, 1.0, 1.25 and 1.5 equivalents of nitric acid (N) with respect to chromium nitrate. Products are designated as N-0.25, N-0.5, N-0.75, N-1.0, N-1.25 and N-1.5 respectively. The sample without HNO_3 or other additives was named N-0. All these experiments were carried out with 1.0 mmol each of chromium(III) nitrate nonahydrate and terephthalic acid in a PTFE- (Teflon-) lined autoclave at 220 °C for 8 hours (see Exp. section). After hydrothermal reaction, the purification of products followed as described in the Exp. section. The analytical results showed that a considerable improvement of yield and product quality could be reached compared to experiments without addition of nitric acid (Table 2).

Table 2 Yield, surface area and pore volume for MIL-101(Cr) with various equivalents of HNO_3 (N) as additive.

HNO_3 (N)-equivalents[a]	Yield (%)[a]	S_{BET} (m²/g)[b]	$S_{Langmuir}$ (m²/g)	V_{pore} (cm³/g)[c]
N-0	56.6	2410	3270	1.30
N-0.25	67.5	2740	3600	1.33
N-0.5	71.7	2770	3690	1.40
N-0.75	73.6	2890	3910	1.38
N-1.0a	82.3	3450	4610	1.66
N-1.0b[d]	81.6	3130	4330	1.58
N-1.0c[d]	80.8	3420	4640	1.69
N-1.25	69.9	3060	4220	1.52
N-1.5	66.2	2540	3320	1.26

[a] HNO_3 equivalents with respect to Cr and $bdcH_2$. The Cr:bdc ratio is always 1:1, and the yield is based on Cr.

[b] Calculated in the pressure range $0.05 < p/p_0 < 0.2$ from N_2 sorption isotherm at 77 K with an estimated standard deviation of ± 50 m²/g.

[c] Calculated from N_2 sorption isotherm at 77 K ($p/p_0 = 0.95$) for pores ≤ 20 nm.

[d] Repeated experiments to demonstrate reproducibility.

Nitrogen sorption isotherms of HNO_3-variable MIL-101(Cr) are shown in Fig. 2, which are typical type I sorption isotherms[65] as reported in the literature for MIL-101(Cr).[15] Obviously, MIL-101(Cr) with one equivalent of HNO_3 (N-1.0, red curve) possesses the highest Brunauer Emmett Teller (BET) surface area (3450 m²/g). With less or more HNO_3 equivalents the surface area decreases. Fig. 2 also shows the curve of HNO_3 equivalents versus the corresponding S_{BET} value. It is obvious that the addition of 1.0 equivalent of nitric acid in synthesis produced the best porosity of MIL-101(Cr). In addition, N-1.0 gave an excellent high yield around 80% after product purification (Table 2). Additionally, N-0.25, N-0.5, N-0.75, N-1.25 and N-1.5 also showed a significant increase in yields compared to the original literature yield by Férey *et al.*[15] Analysis of the literature (Table 1) shows that only the use of TMAOH as a basic modulator might give comparable yields and quality in porosity of the material, however, this claim is yet to be proven, as there are two reports indicating much lower yields under comparable conditions (Table 1).

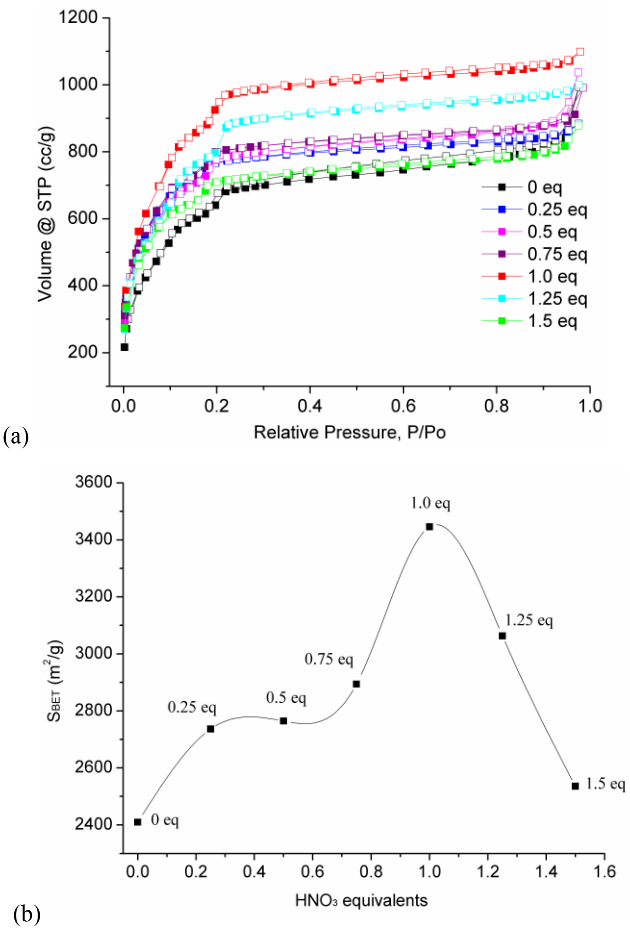

Fig. 2 (a) N_2 adsorption−desorption isotherms of HNO_3-variable MIL-101(Cr); filled symbols are for adsorption, empty symbols for desorption. (b) Plot of S_{BET} values versus HNO_3 equivalents.

To confirm that the experiment N-1.0 can be reproduced, two repeated experiments were carried out. The results are also included in Table 2. Overall, the synthesis with 1.0 eq. of HNO_3 is reproducible with yields above 80% and BET surface areas above 3100 m^2/g. The nitrogen sorption isotherms of each repeated experiment can be found in Fig. S2 in ESI†. Yields and surface areas are near the high end of syntheses reported in the literature (Table 1).

Furthermore, higher equivalents of nitric acid (2.0 eq. and 5.0 eq.) were also tested in MIL-101(Cr) synthesis. However, under too high nitric acid concentration condition, there is no positive effect anymore. In the 2.0 eq. experiment, S_{BET} decreased to 1990 m²/g, while 5.0 eq. gave a grey powder product without porosity. Thus, in a small-scale MIL-101(Cr) synthesis (5 mL scale), using 1.0 eq. HNO_3 is the optimum quantity.

The purity of N-1.0 was analyzed by CHN and EDX elemental analysis. Before elemental analysis, N-1.0 was dried in a vacuum oven (120 °C, 12 mbar) for 2 h. Calcd. for $[Cr_3(O)(OH)(bdc)_3(H_2O)_2]\cdot 2H_2O$: C 38.26, H 2.81, N 0, Cr 20.70; found C 38.43, H 2.91, N 0.00. From EDX analysis, the atom ratio C/Cr = 8.5 (calc. 8.0) is in good agreement with the formula.

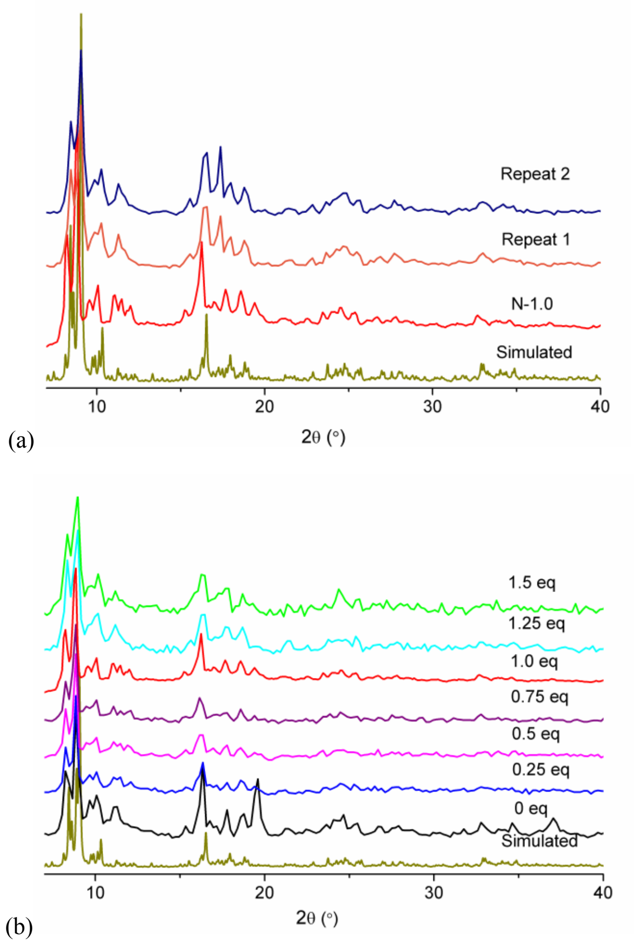

Fig. 3 Powder X-ray diffractograms of (a) N-1.0 samples and (b) samples with other HNO_3 equivalents in comparison to simulated pattern (Cu-Kα radiation).

The powder X-ray diffractograms of the MIL-101(Cr) samples with HNO_3 as an additive can all be positively matched to the simulated XRD pattern which was generated from the deposited X-ray data file at the Cambridge Structure Database (CSD-Refcode OCUNAK) using the program MERCURY (Fig. 3).

The pore size distribution curve and cumulative pore volume curve for N-1.0 were analyzed by NL-DFT method (Fig. S3 in ESI†) and are similar to the reported pore size distribution for MIL-101(Cr).[66,67,68]

Upscaling the synthesis of MIL-101(Cr)

Another objective of this work was to transfer the synthesis of MIL-101(Cr) to larger scale of about 100 g product in a single batch. Therefore, the scale-up to a reaction volume of 3 L (see 3 L autoclave in Fig. S4 in ESI†) was successively investigated and achieved. According to the resulting analytical data the procedure for the synthesis of MIL-101(Cr) was adapted and optimized as follows to produce the material in good quality and quantity.

In the literature the MIL-101 synthesis at smaller scales was conducted without stirring.[69,70,71] Since the reaction volume was substantially increased, it was interesting to see, whether stirring would be required in larger scale reactions to maintain homogeneity for the formation of the desired product. The results of the experiments indicate that stirring of the reaction mixture seems not to be necessary to form MIL-101(Cr) in good quality. In fact, stirring leads to a material that showed a lower BET surface area (Fig. 4).

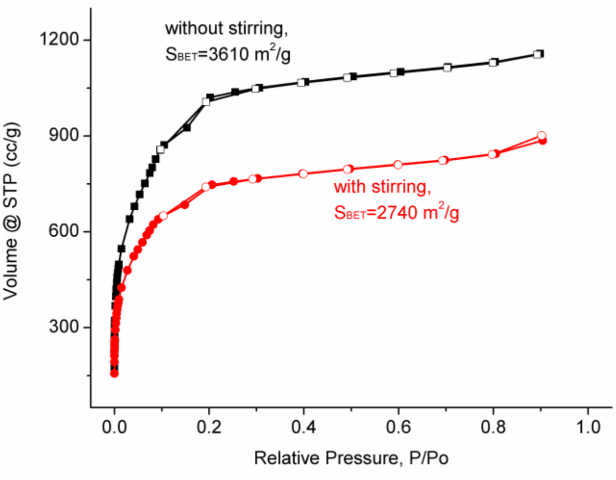

Fig. 4 Nitrogen sorption isotherms and their corresponding BET surface area for non/stirring-experiments of large-scale preparations of MIL-101(Cr), filled symbols are for adsorption, empty symbols for desorption. The synthesis and treatment of the products both followed the general procedure. The BET surface areas were calculated in the pressure range $0.05 < p/p_0 < 0.2$ from N_2 sorption isotherms at 77 K with an estimated standard deviation of ± 50 m^2/g.

Also, the influence of the reaction temperature on the resulting material was studied. Experiments at smaller scales are usually conducted at 220 °C (Table 1). A series of runs were carried out that covered a temperature range from 180–220 °C. The results suggested that a lower reaction temperature also forms the desired product in good quality. Unexpected was the observation, that a reaction temperature of 220 °C at a larger scale seemed to produce an unknown phase instead of the intended MIL-101(Cr) product (Fig. 5). This result also indicated that in the case of large scale synthesis, the optimized condition can be different from small scale synthesis.

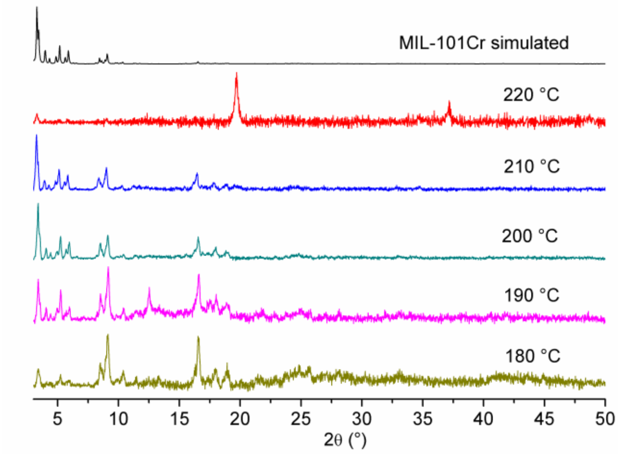

Fig. 5 PXRD of large-scale preparations of MIL-101(Cr) at different temperatures. (Diffractograms were recorded on a Bruker D8 Advance with DaVinci™, Cu-Kα radiation) .

In addition the reaction time (6-16 h) and cooling time (4-24 h) were extended to study their impacts on the resulting material and yield in the large-scale synthesis. The results indicated no significant effect of reaction and cooling time on quality and quantity of the resulting material. A possible explanation is that crystallization takes place very quickly. Once the material crystallizes, there is only a minor equilibrium process of dissolution and recrystallization.

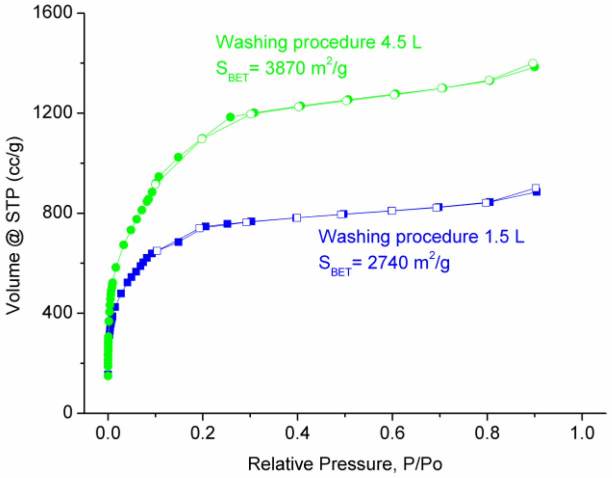

Fig. 6 N_2 sorption isotherms and BET surface area of materals from large scale synthesis and different washing procedures. The noted procedure "1.5 L - blue" ("4.5 L – green") refers to washing with 1.5 L (4.5 L) DMF – separation – 1.5 L (4.5 L) ethanol – separation – 1.5 L water; see Exp. section for details of the 4.5 L procedure.

Furthermore an optimized washing procedure was established for large-scale synthesis. In the initial procedure the raw product was suspended in DMF by using half of the reaction volume, that is, 1.5 L, stirred for 15 min. and isolated by centrifugation. This washing procedure was repeated with 1.5 L ethanol and 1.5 L water. Using this procedure we obtained a material with considerable amounts of impurities still remaining in the pores of the product. Hence, we decided to prolong the washing step and to employ solvent volumes 1.5 times of the reaction volume (*i.e.* 4.5 L) to ensure the removal of impurities from the pores. The product obtained after washing according to the new procedure (for details see Exp. section) gave materials with higher purity. Consequently, increased nitrogen sorption capacity was observed for all materials after using the new washing procedure (Fig. 6). The method proved to be very efficient to remove starting material or impurities that remained in the pores of the product. For a large-scale product the BET surface of 3870 m^2/g can be considered remarkable.

Finally, the addition of 0.5, 1.0 and 1.5 HNO_3 equivalents with respect to chromium nitrate was investigated (Fig. 7). The experiments confirmed the results of the small scale reactions, in which the yield was considerably improved by the addition of nitric acid. The large scale preparations also gave about 20% more material for all conducted experiments with addition of nitric acid (0.5, 1.0 and 1.5 eq.) compared to experiments without addition of nitric acid. We assume that the addition of nitric acid affects the particle growth, yielding material with larger particle size, thus, leading to material that is more efficiently isolated by centrifugation (centrifugation is a major issue in large-scale preparation). The yields were around 48% for experiments without addition of nitric acid. Addition of nitric acid gave yields around 66% (for 0.5 eq), 68-72% (for 1.0 eq) and 67% (for 1.5 eq).

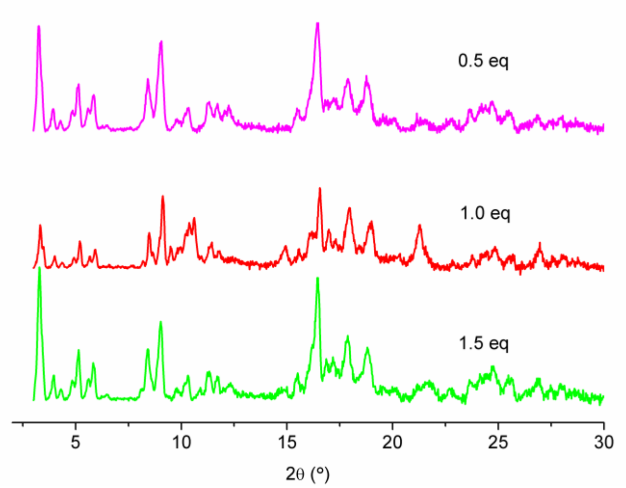

Fig. 7 PXRD of large-scale preparations of MIL-101(Cr) with different equivalents HNO_3. (PXRD data were recorded on a Bruker D8 Advance with DaVinci™, Cu-Kα radiation).

Low temperature synthesis of MIL-101(Cr) with acetic acid

Normally, MIL-101(Cr) syntheses are carried out at 220 °C in a Teflon liner within autoclaves. Using microwave irradiation as heating source one can decrease the reaction temperature to 210 °C.[72] Using TMAOH as mineralizing agent and prolonging the reaction time to 24 h one can reduce the reaction temperature to 180 °C. But until now we are not aware of a report to obtain MIL-101(Cr) at a temperature below 180 °C. We have also tested the additions of several other inorganic and organic acids in MIL-101(Cr) synthesis (see Table 5 below). Among them, acetic acid shows a special effect in so far, that it can largely decrease the reaction temperature without significant influence on the porosity of the material. A lower synthesis temperature can be desired not only from an energetic point of view, but also, e.g., when MIL-101(Cr) is intended as a host for sensitive guest molecules.[48,49,50,51] In cases, where S_{BET} of MIL-101(Cr) is only 2000 m²/g, there is still enough space for the storage of guest molecules.[73] Porosity of the MIL-101 material is not the only consideration, but a lower synthesis temperature may allow for the inclusion of temperature-sensitive molecules during the *in-situ* formation of MIL-101(Cr). For example, one could directly synthesize MIL-101(Cr) in the presence of guest molecules at lower temperature. With the addition of acetic acid, the MIL-101(Cr) synthesis temperature can be decreased to as low as 160 °C. In some experiments, the addition of several milligrams of pre-formed MIL-101(Cr) seeding powder was necessary.

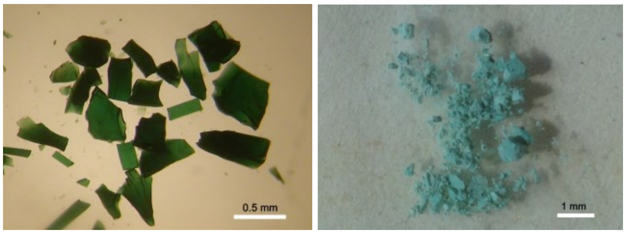

Fig. 8 Image of MIL-101(Cr) with acetic acid (8.3 equivalents, 220 °C) (left) and HNO_3 (N-1.0) (right) as modifier.

When 1 equivalent of acetic acid with respect to chromium nitrate was added in the MIL-101(Cr) synthesis at 220 °C, the product is of competitive purity, yield and BET surface relative to other MIL-101(Cr) products. If the quantity of acetic acid is increased up to 8.3 equivalents with respect to chromium, a green glassy-looking material was formed (Fig. 8, left). When the equivalent of addition of acetic acid with respect to chromium is lower than 8.3, the product is a green powder (similar to N-1.0 in Fig. 8, right). Upon addition of more than 8.3 equivalents of acetic acid with respect to chromium no product was isolated. The yield and porosity information of acetic acid-variable MIL-101(Cr) are listed in Table 3. Powder X-ray diffractograms of MIL-101(Cr) with acetic acid can be positively matched to the simulated pattern of MIL-101(Cr) (Fig. 9).

Table 3 Yield, surface area and pore volume for MIL-101(Cr) with various equivalents of acetic acid as additive.

Acetic acid equivalents[a]	Yield (%)[a]	S_{BET} (m²/g)[b]	$S_{Langmuir}$ (m²/g)	V_{pore} (cm³/g)[c]
1 eq	65.3	2680	3490	1.17
2 eq	52.1	2450	3210	1.28
5 eq	36.4	2660	3480	1.27
8.3 eq	24.4	2750	3620	1.55
10 eq	none	--	--	--

[a] Acetic acid equivalents with respect to Cr and $bdcH_2$. The Cr:bdc ratio is always 1:1, and the yield is based on Cr. The reaction temperature was 220 °C. No seed crystals were added – different from reactions in Table 4.

[b] Calculated in the pressure range $0.05 < p/p_0 < 0.2$ from N_2 sorption isotherm at 77 K with an estimated standard deviation of ± 50 m²/g.

[c] Calculated from N_2 sorption isotherm at 77 K ($p/p_0 = 0.95$) for pores ≤ 20 nm.

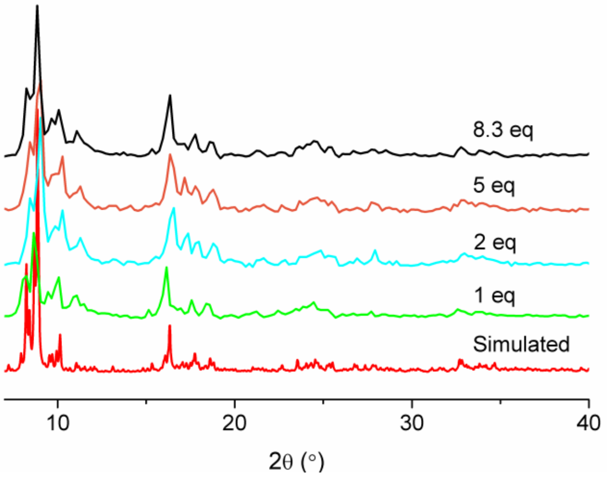

Fig. 9 The PXRD patterns of acetic acid-variable MIL-101(Cr) compared with simulated pattern (Cu-Kα radiation).

MIL-101 formed with 1 eq. and 8.3 eq. acetic acid had BET surface areas of 2680 m²/g and 2750 m²/g respectively. Considering literature reports of MIL-101 with surface areas in the range of 2000-3000 m²/g (Table 1), these values are acceptable. The synthesis of MIL-101Cr with 8.3 eq. of acetic acid was also carried out at temperatures of 220, 200, 180 and 160 °C (Table 4). Upon lowering the temperature, the yield decreased considerably. We found, however, that the addition of about 5 milligrams of pre-formed MIL-101(Cr) powder as seeds would significantly raise the yield again (Table 4). The PXRD patterns of the "seeded" samples are in good agreement with the simulated pattern of MIL-101(Cr) (Fig. 10). The BET results of these "seeded" samples are also better than those of the "non-seeded" samples (Table 4).

Noteworthy, the BET and porosity results did not show a clear dependence on temperature. For example, a material obtained from a non-seeded synthesis at 180 °C with low-yield had the highest BET surface area of 3240 m^2/g (Table 4). For the nitrogen sorption isotherms of "seeded" samples at different synthesis temperature see Fig. S5 in ESI†.

Table 4 Yields, surface area and pore volume for MIL-101(Cr) with acetic acid as additive at different temperature and seeding/non-seeding.

Acetic acid equivalents[a]	Seeded	Temp. (°C)	Yield (%)[a]	S_{BET} $(m^2/g)^b$	$S_{Langmuir}$ (m^2/g)	V_{pore} $(cm^3/g)^c$
A-8.3-220	No	220	24.4	2750	3620	1.55
A-8.3-200	No	200	24.4	2360	3060	1.31
A-8.3-180	No	180	13.2	3240	4400	1.61
A-8.3-160	No	160	none	—	—	—
A-8.3-220s	Yes	220	48.9	2810	3680	1.85
A-8.3-200s	Yes	200	44.5	2790	3600	1.30
A-8.3-180s	Yes	180	43.2	2750	3630	1.30
A-8.3-160s	Yes	160	33.5	2700	3500	1.38

[a] Acetic acid equivalents with respect to Cr and $bdcH_2$. The molar Cr:bdc ratio is always 1:1 with 1.0 mmol (400 mg) $Cr(NO_3)_3 \cdot 9H_2O$ and 1.0 mmol (166 mg) of $bdcH_2$, and the yield is based on Cr.

[b] Calculated in the pressure range $0.05 < p/p_0 < 0.2$ from N_2 sorption isotherm at 77 K with an estimated standard deviation of ± 50 m^2/g. Nitrogen sorption isotherms of the seeded samples are presented in Fig. S5 in ESI†.

[c] Calculated from N_2 sorption isotherm at 77 K ($p/p_0 = 0.95$) for pores ≤ 20 nm.

It is worth to note that the presence of seeds in the synthesis of MIL-101(Cr) allowed a temperature as low as 160 °C at which no product was obtained without seeds. At temperatures below 160 °C no MIL-101(Cr) products could be obtained anymore even if seeding was applied.

The purity of A-8.3-160 was analyzed by CHN and EDX elemental analysis. Before analysis, A-8.3-160 was dried in a vacuum oven (120 °C, 12 mbar) for 2 h. Calcd. for $[Cr_3(O)(OH)(bdc)_3(H_2O)_2]\cdot 2H_2O$: C 38.26, H 2.81, N 0.00; found C 37.92, H 2.65, N 0.00. From EDX analysis, the atom ratio C/Cr = 7.7 (calc. 8.0) is in good agreement with the formula.

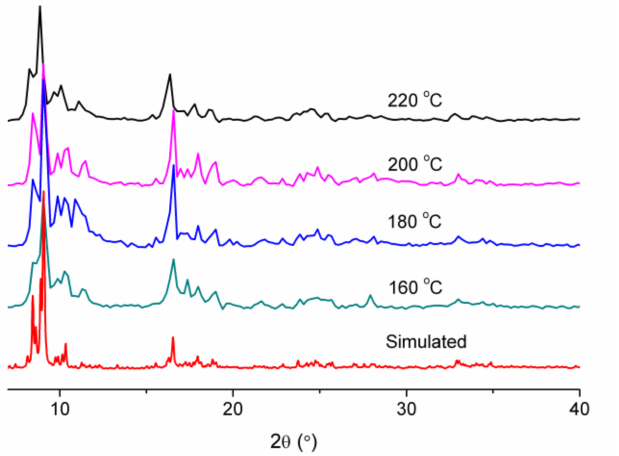

Fig. 10 Powder X-ray diffractograms of "seeded" samples with 8.3 eq. of acetic acid at different temperature compared with simulated MIL-101(Cr) pattern.

Other acids as modifiers in MIL-101(Cr) synthesis

We also compared the use of hydrofluoric acid, trifluoroacetic acid, sulfuric acid, hydrochloric acid, phenylphosphonic acid, benzoic acid, formic acid, fumaric acid, citric acid and succinic acid as modifiers in MIL-101(Cr) synthesis (Table 5).

Table 5 Yields and porosity information of MIL-101(Cr) with different acid additives.

Additive/Modifier [a]	Yield (%)[a]	S_{BET} $(m^2/g)^b$	$S_{Langmuir}$ (m^2/g)	V_{pore} $(cm^3/g)^c$
Hydrofluoric acid	47.4	3620	4990	1.82
none	56.6	2410	3270	1.30
(sorted by approximate acid strength)				
Hydrochloric acid	36.3	1560	2030	0.79
Sulfuric acid	48.2	1750	2200	0.81
Nitric acid (N-1.0a)	82.3	3450	4610	1.66
Trifluoroacetic acid	73.8	2650	3620	1.34
Phenylphosphonic acid	51.9	2460	3350	1.49
Fumaric acid	28.7	760	1040	0.69
Citric acid	37.2	740	1050	0.58
Formic acid	27.1	590	720	0.56
Succinic acid	59.8	2510	3250	1.28
Benzoic acid	39.4	1760	2290	0.93
Acetic acid (8.3 eq)	24.4	2750	3620	1.55

[a] The quantities of all additives were 1.0 equivalent with respect to chromium. The Cr:bdc ratio is always 1:1, and the yield is based on Cr. All products were purified in the same way as described in the experimental section.

[b] Calculated in the pressure range $0.05 < p/p_0 < 0.2$ from N_2 sorption isotherm at 77 K with an estimated standard deviation of ± 50 m^2/g.

[c] Calculated from N_2 sorption isotherm at 77 K ($p/p_0 = 0.95$) for pores ≤ 20 nm.

The addition of HF was used to repeat the original experiment.[15] Indeed, using HF as an additive yielded a MIL-101(Cr) product with the highest BET surface area of all small-scale samples and a yield of around 50%, very near to the values reported in the literature (cf. Table 1).[15] An additive-free method gave only 2410 m^2/g of BET surface area and the yield was similar to the HF-experiment. The PXRD patterns (see Fig. S6 in ESI†) of the products with the various additives showed more or less byproduct formation. Fumaric and citric acid failed to function as sensible additives.

Conclusions

In summary, only nitric acid (HNO_3) and acetic acid (CH_3COOH) proved advantageous in the synthesis of MIL-101(Cr) from a series of tested mineral and organic acid additives/modifiers as alternatives to HF. An advantage of HNO_3 was a >30% increase in yield with the BET surface area (>3100 m^2/g) lagging only ~10% behind compared to the use of HF. Nitric acid also worked well in large-scale MIL-101(Cr) synthesis (3 L) where the toxic nature of HF would be of increased concern. The combined use of acetic acid and seeding of the reaction mixture with MIL-101(Cr) allowed to decrease the temperature of the synthesis to 160 °C, retaining a yield of ~50% and acceptable BET surface area 2700-2800 m^2/g. The demonstrated singularly low temperature synthesis broadens the range of synthetically tolerable conditions for potential functional guests, which could be embedded in MIL-101(Cr).

Experimental Section

Materials: Chromium(III) nitrate nonahydrate (98.5%, Alfa Aesar or 99%, Acros), benzene-1,4-dicarboxylic acid, terephthalic acid ($bdcH_2$, 99+%, Acros), nitric acid (65wt%, VWR or . p. A. Applichem), acetic acid (99.7+%, Alfa Aesar), hydrofluoric acid (48 wt. % in H_2O, Sigma-Aldrich), sulfuric acid (95.0%-98.0%, Sigma-Aldrich), hydrochloric acid (36 wt. % in H_2O, Alfa Aesar), trifluoroacetic acid (99%, Sigma-Aldrich), phenylphosphonic acid (98%, Sigma-Aldrich), benzoic acid (99.5%, Sigma-Aldrich), formic acid (97%, Alfa Aesar), fumaric acid (99.0%, Fluka), citric acid (99.5%, Sigma-Aldrich), succinic acid (99.5%, Fluka), *N,N*-dimethylformamide (DMF, 99%, VWR or Alfa Aesar) and ethanol (99.8%, Carl Roth or p.a. Applichem). All chemicals were used as obtained from commercial sources without further purification.

Instrumentation

Powder X-ray diffraction (PXRD) measurements were carried out for Figures 3, 9 and S6 on samples at ambient temperature with a Bruker D2 Phaser using a flat silicon, low background sample holder and Cu-K_α radiation (λ = 1.54184 Å) at 30 kV and 0.04°/s. Diffractograms were obtained on flat layer sample holders where at low angle the beam spot is strongly broadened so that only a fraction of the reflected radiation reaches the detector which leads to the low relative intensities measured at $2\theta < 7°$. Simulated PXRD pattern were calculated from single crystal data with the MERCURY 3.0.1 software suite from CCDC. For Figures 5 and 7 he PXRD data was recorded on a Bruker D8 Advance with DaVinci™, using a rotating sample holder, a Cu anode tube at 40kV/40mA, with a Ni filter and constant sample illumination spot size (broadness: 12 mm); step size 0.02°, 0.2 s/step, Cu-Kα radiation.

Nitrogen physisorption isotherms at 77 K were obtained using a NOVA-4000e instrument for Figure 2, S2, S5, Table 2 to Table 5 within a partial pressure range of 10^{-6}~1.0. Before measurements, the samples were degassed at 120 °C for 2 h. Alternatively, nitrogen sorption isotherms were measured at 77 K using a Quantachrome Autosorb iQ MP gas sorption analyzer for Figure 4 and 6. Ultra high purity (UHP, grade 5.0, 99.999%) nitrogen, and helium gases were used; the latter was used for performing cold and warm free space correction measurements. Samples were degassed for 2 h at 120 °C with the built-in oil-free vacuum system of the instrument (ultimate vacuum <10^{-8} mbar).

The samples were transferred to pre-weighed sample tubes capped with a septum. Then the sample tube was connected to the preparation port of the sorption analyzer and degassed under vacuum for the specified time and temperature. After weighing, the sample tube was then transferred to the analysis port of the sorption analyzer. Helium gas was used for the determination of the cold and warm free space of the sample tubes. DFT calculations for the pore size distribution curves were carried out with the native ASiQWin 1.2 software employing the 'N_2 at 77 K on carbon, slit pore, NLDFT equilibrium' model.[74,75,76]

Elemental (C, H, N) analysis was done with a Perkin-Elmer Series 2 Elemental Analyser 2400.

Energy dispersive X-ray spectrometric (EDX) measurements were carried out on a Jeol scanning electron microscope JSM-6510 with tungsten (W) cathode and EDX unit. The samples were coated with Au for 20 sec at 30 mA by a Jeol JFC-1200 sputter (JSM-6510).

Small-scale synthesis and purification of MIL-101(Cr) (general procedure)

A typical synthesis involves a solution containing chromium (III) nitrate $Cr(NO_3)_3 \cdot 9H_2O$ (400 mg, 1.0 mmol), the chosen additive acid (1.0 mmol) and benzene-1,4-dicarboxylic acid H_2bdc (164 mg, 1.0mmol) in 5 mL H_2O. The mixture is transferred to the PTFE/Teflon liner in a hydrothermal autoclave which is heated for 8 h at 220°C and cooled afterwards slowly to room temperature at a rate of 30 °C /h in 6 h.

The contents of the autoclave were transferred to two centrifuge tubes and the supernatant solution was carefully removed after centrifugation. Water (5 mL) was added in each tube and the solid was evenly dispersed in the aqueous phase. After renewed centrifugation and removal of the supernatant solution, DMF (5 mL) was added to each tube which was placed in a hot (80 °C) ultrasonic bath and sonicated for 1 h. Centrifugation was again used to separate MIL-101 and DMF. The precipitate was transferred in a 25 mL beaker where it was stirred with 10 mL of water at 70 °C for 5 h. After separation by centrifugation, the same washing procedure but using ethanol was repeated once more at the same temperature. The final product was obtained by centrifugation and dried in a vacuum oven (120 °C, 12 mbar) for 2 h.

Large-scale synthesis and purification of MIL-101Cr (general procedure)

Chromium(III) nitrate nonahydrate (192 g, 0.48 mol), terephthalic acid (81.3 g, 0.49 mol) and conc. nitric acid (0.49 mol) were stirred in water (2.4 L) and transferred into a 3 L autoclave. The suspension was heated to 200 °C and left unstirred for 15 h. The mixture was cooled to 20 °C within 24 h. After cooling the suspension was filled into centrifuge vessels. The solid was isolated by centrifugation (4700 U/min for 30 min). The supernatant liquid phase was discarded and the resulting solid was stirred in DMF (4.5 L) for one hour. The suspension was then again centrifuged (4700 U/min for min). The supernatant liquid phase was discarded and the solid stirred in DMF (4.5 L, 16 h). The solid was isolated by centrifugation and the washing step was repeated with ethanol (4.5 L, 1 h and 4.5 L, 16 h of stirring). After the final isolation the resulting wet solid was dried for 2 d in air at room temperature. The dried solid was crushed to a homogenous powder and dried for another 2 d in air at room temperature to produce MIL-101(Cr) as a green powder. Yield 127.1 g (68% with respect to chromium). Analyses of the product were carried out by elemental analysis, powder X-ray diffraction and N_2 sorption, see above.

Acknowledgements

The work was supported by the Federal German Ministry of Economics (BMWi) under grant 0327851A/B/C. T. Z. thanks the China Scholarship Council (CSC) for a doctoral fellowship and I. B. thanks the Alexander von Humboldt foundation for a postdoctoral fellowship.

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† Electronic Supplementary Information (ESI) available: Graphics of MIL-101(Cr) structure elements; additional N_2 sorption isotherms, pore size distribution curves, powder X-ray diffractograms, picture of 3 L autoclave. See DOI: 10.1039/b000000x/

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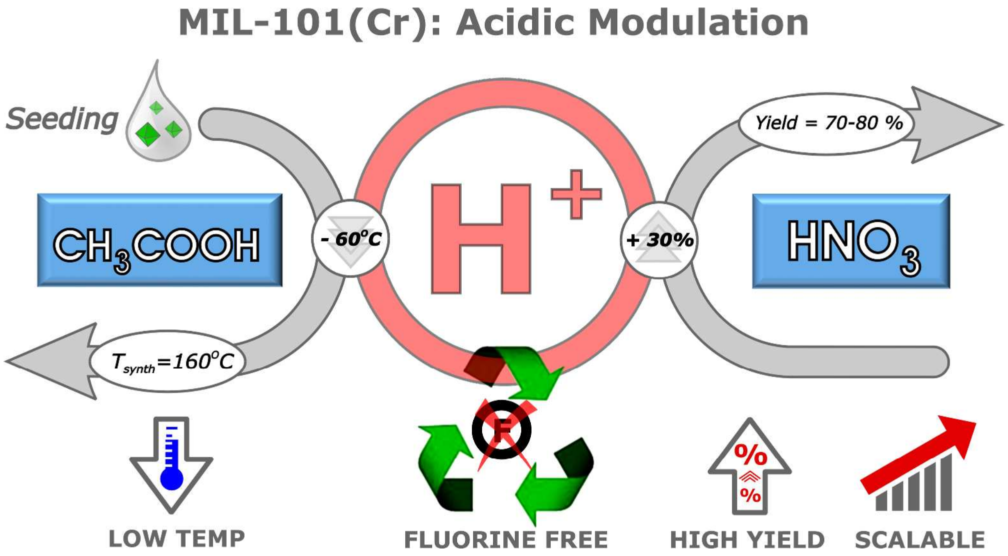
MIL-101(Cr): Acidic Modulation
Seeding
CH3COOH
- 60°C
H+
+ 30%
HNO3
Yield = 70-80 %
Tsynth=160°C
F
%
%
LOW TEMP
FLUORINE FREE
HIGH YIELD
SCALABLE