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Communication

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Synthesis Modulation as a Tool To Increase the Catalytic Activity of Metal–Organic Frameworks: The Unique Case of UiO-66(Zr)

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Supporting Information

ABSTRACT: The catalytic activity of the zirconium terephthalate UiO-66(Zr) can be drastically increased by using a modulation approach. The combined use of trifluoroacetic acid and HCl during the synthesis results in a highly crystalline material, with partial substitution of terephthalates by trifluoroacetate. Thermal activation of the material leads not only to dehydroxylation of the hexanuclear Zr cluster but also to post-synthetic removal of the trifluoroacetate groups, resulting in a more open framework with a large number of open sites. Consequently, the material is a highly active catalyst for several Lewis acid catalyzed reactions.

Researchers have high expectations for metal–organic frameworks (MOFs) in catalysis because of the high concentration of metal ions dispersed in a micro- or mesoporous matrix.[1] However, the activity of current MOFs rarely approaches that of other microporous solids, e.g., zeolites.[2] One option to overcome this low activity is the activation of dormant, fully coordinated framework metal ions, which are unavailable for catalysis. While in some cases the reactants seem to break the metal–linker bonds,[3] the most catalytically active MOFs typically remain those with structural coordinatively unsaturated Lewis acid sites.[1] Recently, several tools were proposed to increase the catalytic activity of MOFs. For instance, post-synthetic treatment of MIL-100(Fe) with inorganic acids increases the number of Lewis and Brönsted acid sites, resulting in higher activity and selectivity in Diels–Alder reactions.[4] For MOF-5, Ravon et al. found that materials prepared through fast precipitation were the most active ones in alkylations, which was ascribed to a large number of OH groups at structural defects.[5] In this Communication, we show how the use of specific synthesis modulators allows for a high level of control over the number and nature of the defect sites in the well-studied zirconium terephthalate MOF UiO-66 and results in large increases of the catalytic activity.

In MOF preparation, a modulator has typically the same or a similar chemical functionality as the linker molecules, but it is monofunctional rather than bi- or polycipital. The term "coordination modulation" was coined in 2009 by the group of Kitagawa, who used modulators as a tool for controlling size and shape of $[\{Cu_2(NDC)_2(dabco)\}]_n$[6] and HKUST-1 crystals;[7] however, earlier, similar examples can be found as well.[8] Besides organic carboxylic acids, also organic bases or even inorganic modulators can exert analogous effects.[8d,9] For the zirconium dicarboxylate MOFs, modulators like acetic acid were introduced by Schaatte et al.[10] in the synthesis of UiO-66 and UiO-67. In these cases, the role of the modulator is primarily to terminate the structure. However, a study of the copper carboxylate MOF PCN-125 shows that a modulator may also be incorporated inside the crystals. Thus, partial replacement of the terphenyl-3,3″,5,5″-tetracarboxylate linker by functionalized isophthalic acid resulted in the creation of functionalized mesopores.[11]

Recently, we demonstrated that the unexpected catalytic activity[12] of the seemingly coordinatively saturated UiO-66[13] is due to missing linkers in the structure.[14] Additionally, the activity of the material can be significantly increased by using electron-withdrawing groups on the terephthalate linkers.[15] Here we demonstrate how the correct use of modulators, like trifluoroacetic acid, can create even much more active materials.

UiO-66 was synthesized from a mixture containing equimolar amounts of $ZrCl_4$, terephthalic acid (BDC), and H_2O in *N*,*N*′-dimethylformamide (DMF), with addition of different equivalents (X) of trifluoroacetic acid (TFA) (hereafter noted as UiO-66-X) with respect to the other reactants (e.g., BDC). As modulators are expected to facilitate crystallization for a variety of MOFs,[7,8,10] it is not surprising that the diffractograms show well-resolved signals, indicating that the crystallinity of UiO-66-X is maintained, if not even improved, when more TFA is added (Figure S1). Unlike benzoic, acetic, or formic acid, however,[10] TFA does not affect the crystal size (Figure S3): use of TFA as a modulator leads to the same morphology of small (~300–600 nm) intergrown particles as in the non-modulated synthesis.

The catalytic activity of UiO-66 synthesized with different concentrations of modulator (0–20 equiv of TFA with respect to BDC) was tested using the "ene"-type cyclization of citronellal to isopulegol. All catalysts were activated under

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vacuum at 320 °C for 12 h to ensure full dehydroxylation of the inorganic cluster. From a screening of monocarboxylic acids with different pK_a's, CF_3COOH was found to be the modulator giving by far the most active materials (see also Supporting Information, Table S1). Conversion plots are given in Figure 1.

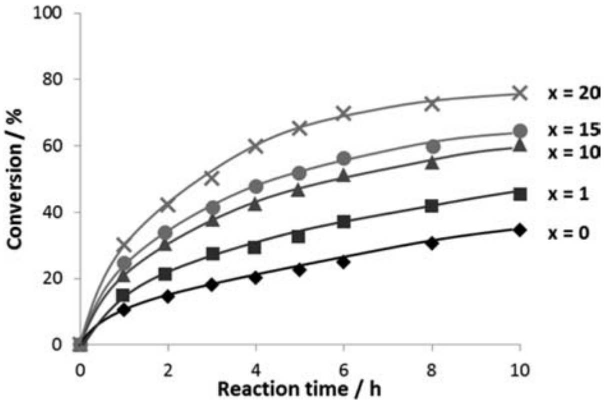

Figure 1. Conversion of citronellal over UiO-66-X vs time (toluene, 110 °C, citronellal:Zr^{4+} = 15).

The addition of small quantities of TFA to the synthesis already significantly increases the activity; a maximum activity is obtained using materials synthesized with 20 equiv of TFA. While regular UiO-66 reaches a conversion of 34% after 10 h, UiO-66-20 has converted almost 75% of citronellal after the same time. The selectivity toward isopulegol, which directly reflects Lewis acid strength,[15] fluctuates for all (non)modulated materials between 75 and 77%. This proves that the increase in activity is due to the creation of a larger number of open sites, rather than to a modified acid strength. The use of even larger quantities of TFA during synthesis did not result in more active materials.

In addition to the use of CF_3COOH as a modulator, the effect of adding HCl as a crystallizing agent was investigated. The literature contains a wide variety of recipes to synthesize UiO-66, with differences in concentrations, solvent, and with addition of inorganic bases or acids. In the synthesis described by Yang et al.,[16] 1 equiv of HCl is added to the synthesis mixture to facilitate the upscaling. During crystal formation, HCl has a double function: it slows down the hydrolysis of $ZrCl_4$ and counteracts the deprotonation of the dissolved carboxylic acids. Consequently, in a mixture containing both TFA and BDC, HCl favors the competitive incorporation of trifluoroacetate. To assess the effect of added HCl on the catalytic activity, UiO-66 and UiO-66-10 were synthesized with the addition of 1 equiv of HCl (indicated as UiO-66_{HCl} and UiO-66-10_{HCl}). Catalytic tests show that this addition of HCl to the synthesis has a strong effect on the activity of the TFA modulated material (Figure 2). The conversion of citronellal after 1 h reaches almost 40% with UiO-66-10_{HCl}, whereas UiO-66-10 reaches a conversion of 21%. Strikingly, the use of HCl has almost no effect on the activity of the non-modulated materials.

To rationalize these observations, one needs to understand the role of TFA during framework formation. The facile deprotonation of the strongly acidic TFA suggests that trifluoroacetate may be incorporated not only at the crystal boundaries but also even on the hexanuclear cluster inside the structure, instead of a terephthalate linker. The resulting charge imbalance on the opposing cluster may be balanced by replacement of an OH^- group of the $[Zr_6(OH)_nO_{8-n}]^{(8+n)+}$ cluster ($n = 4$ for the ideal structure) by an O^{2-} group, resulting in $n < 4$. Because of the volatile and labile nature of TFA (bp = 72 °C), one may also remove the trifluoroacetate with a thermal treatment, creating even more open sites.

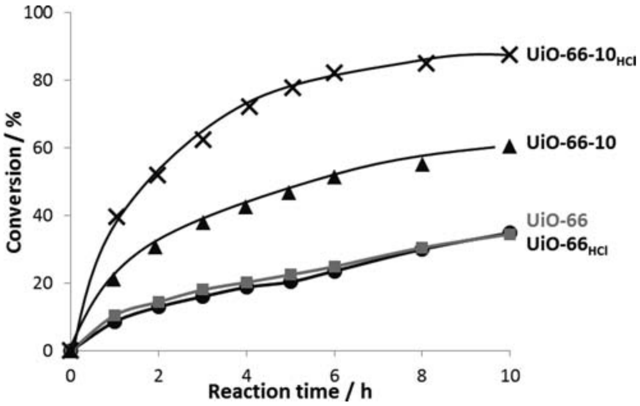

Figure 2. Conversion of citronellal with UiO-66-X synthesized with and without HCl vs time (toluene, 110 °C, citronellal:Zr^{4+} = 15).

To validate such ideas, the model materials UiO-66-10_{HCl} and UiO-66_{HCl} were properly characterized using thermogravimetric analysis (TGA), ^{19}F NMR, FTIR, CD_3CN chemisorption, and N_2 physisorption. In the TGA of UiO-66_{HCl} (Figure S6), the weight loss between 400 and 500 °C is consistent with a BDC:Zr_6 ratio of 5, in line with the known linker deficiency even in well-crystallized materials.[14] The charge imbalance created by the linker deficiencies could be compensated by Cl^- anions, as indicated by EDX measurements, or by changes in the cluster itself (vide supra).[17] The same BDC:Zr_6 ratio of 5 is also observed for the UiO-66 material synthesized without HCl. This indicates that HCl alone does not result in the formation of additional active sites, explaining why UiO-66 and UiO-66_{HCl} present the same catalytic activities (Figure 2).

By contrast, for the modulated material UiO-66-10_{HCl}, TGA shows a stepwise weight loss, and ^{19}F solid-state NMR spectra of materials pretreated at different temperatures help in elucidating these steps. The as-synthesized material contains, besides physisorbed TFA (−75 ppm), also trifluoroacetate anions directly bound to the Zr cluster, with an intense, upfield-shifted signal at −78 ppm (Figure 3). When UiO-66-10_{HCl} is

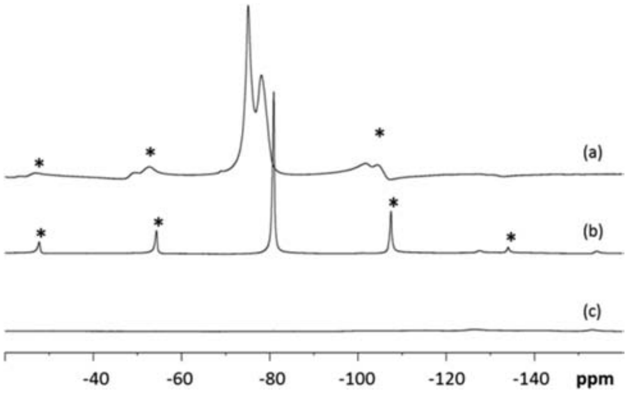

Figure 3. Mass-normalized ^{19}F NMR spectra of (a) UiO-66-10_{HCl} as synthesized, (b) UiO-66-10_{HCl} treated at 200 °C, and (c) UiO-66-10_{HCl} treated at 320 °C. Asterisks indicate spinning sidebands.

heated to 200 °C, the trifluoroacetate remains bound on the cluster; the slight signal shift to −80 ppm and the sharper shape of the signal are probably due to the removal of guest molecules solvating the CF_3 groups. When the material is activated at 320 °C, the fluorine signal is completely lost, revealing that the trifluoroacetates are removed. Nevertheless, the structural order in the material is fully retained (Figure S2).

In the TGA profile of UiO-66-10_{HCl}, the corresponding loss of TFA is discerned as a clear step between 270 and 320 °C. Quantification suggests that, in UiO-66-10_{HCl} treated at 200 °C, the hexanuclear cluster is typically surrounded by one CF_3COO^- and four terephthalate anions, with $[Zr_6O_7(OH)](BDC)_4(CF_3COO)$ as a plausible, correctly charge-balanced formula. As no Cl^- is observed in EDX (see SI), replacement of OH^- ions by O^{2-} ions on the cluster is probably responsible for the charge balance. Such a substantial incorporation of CF_3COO^- proves that the modulator is present not only at the periphery but also in the bulk of the crystal. The process of trifluoroacetate incorporation in UiO-66-10_{HCl} and its loss upon heating was also followed by FTIR (Figure S7). The concentration of OH groups (3670 cm^{-1}) is significantly reduced for UiO-66-10_{HCl} in comparison with UiO-66_{HCl}, confirming that already before the thermal treatment, part of the OH^- ions are replaced by O^{2-} groups to ensure the charge balance. Following diagnostic bands during heating (e.g., at 1638 and ~1200 cm^{-1} for CF_3COO^-) proves the gradual disappearance of the −OH and trifluoroacetate groups. While the dehydroxylation starts at a much lower temperature than the CF_3COO^- removal, the onset of the modulator disappearance coincides with the removal of the last portion of hydroxyl groups (Figure S9). This is an indication that the CF_3COO^- anions recombine with protons from the hexanuclear cluster to allow departure of neutral CF_3COOH, leaving a material with $[Zr_6O_8](BDC)_4$ as a formula.

To quantitatively support these findings, reaction free energies for dehydroxylation and removal of CF_3COOH were obtained using state-of-the-art periodic DFT calculations with the PBE functional in the VASP package, including D3-dispersion corrections (see also SI). The reaction free energy for dehydroxylation amounts to about −74 kJ/mol at 320 °C and 10^{-3} mbar, indicating that the dehydroxylation is easily achieved given the low free energy value. This value remains largely the same for a Zr cluster on which TFA has been incorporated. Removal of CF_3COOH requires a free energy of +24.7 kJ/mol, in line with the higher temperatures (320 °C) needed experimentally for this process. For a partially dehydroxylated cluster, the removal of CF_3COOH is more easily achieved, given the lower free energy of +2.9 kJ/mol. These results indeed confirm that dehydroxylation occurs readily, and that removal of CF_3COOH becomes competitive with water removal at higher activation temperatures.

With only 8 carboxylates surrounding the cluster, rather than 12 in the ideal structure, the question arises whether the loss of these carboxylate groups occurs in an ordered way.[20] High-resolution XRD suggests the carboxylates are missing in a randomized fashion over the length scale of multiple unit cells; the cubic space group *Fm*3*m* still adequately describes the diffraction patterns of materials in the desolvated state (a = 20.76 Å) or after activation at 320 °C (a = 20.69 Å). An ordered linker removal, which still may occur for individual Zr clusters, therefore does not result in a lowering of the overall averaged symmetry which can be observed by XRD.[14] Instead, it can be concluded that linker removal occurs either fully statistically or, as suggested by Valenzano et al.,[14] systematically on a local but not global scale.

To empirically assess the number and strength of the Lewis acid (LA) sites, CD_3CN chemisorption was used, with *in situ* activation at different temperatures prior to the chemisorption. The spectra (Figure S8) show two well-defined signals, at 2260 cm^{-1} for physisorbed CD_3CN and at 2298 cm^{-1} indicative for CD_3CN adsorbed on LA sites. The total number of LA sites at different activation temperatures is given in Figure 4, taking into account a molar absorption coefficient of 3.1 cm/μmol for coordinated species. This immediately shows that the use of TFA strongly increases the number of LA sites in the material. After an activation at 300 °C, UiO-66_{HCl} has 720 μmol/g LA sites, whereas nearly 1100 μmol/g LA sites are present in UiO-66-10_{HCl}. This corresponds to slightly more than two accessible active sites per hexanuclear cluster.

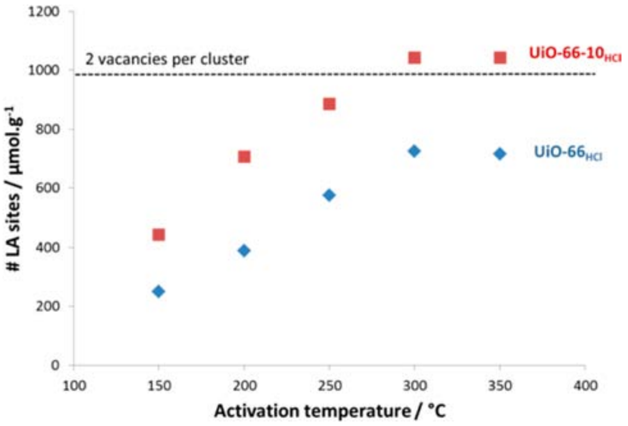

Figure 4. Number of Lewis acid sites as a function of activation temperature.

Consecutive incorporation and loss of TFA not only results in a significantly larger number of open metal sites but also should influence the pore texture. For the non-modulated material (Figure S10), the average pore size matches very well the reported values; however, pore size drastically increases when more TFA is incorporated. In the material with a maximum amount of TFA incorporated (prepared with 20 equiv of TFA with respect to BDC), the pore structure has completely changed from pores of originally 0.78 nm diameter to a material with pores of 1−1.1 nm diameter.

The more open pore structure and the larger number of open sites should make the modulated UiO-66 an excellent catalyst for reactions in which several reactants need to be activated simultaneously, or in which bulky reactants are to be used. As an example, we studied the Meerwein reduction of 4-*tert*-butylcyclohexanone (TCH) with isopropanol (IPA). This reaction requires simultaneous activation of alcohol and ketone to facilitate hydride transfer (Figure 5).

While the non-modulated materials display virtually no activity (respectively 5 and 7% conversion after 24 h for UiO-66 and UiO-66-NO_2), the materials modulated with 10 equiv of TFA display appreciable yields of the *tert*-butylcyclohexanol. However, UiO-66-NO_2 prepared using HCl and TFA is the best catalyst, reaching 93% conversion. Clearly, the increased space around the cluster facilitates the simultaneous activation of the reactants, while the electronic effect of the nitro group is also clear in this reaction.

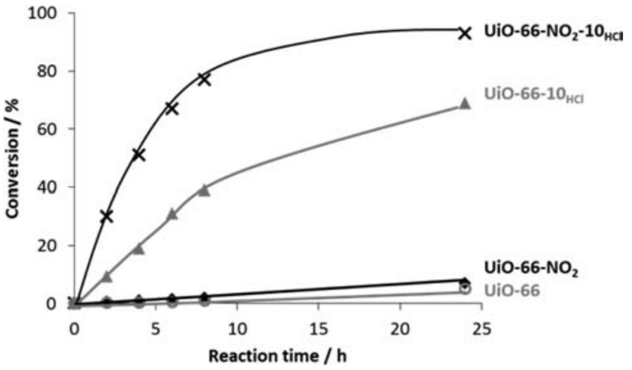

Figure 5. Conversion of TCH over UiO-66-X and UiO-66-NO_2-X vs time (toluene, 100 °C, TCH:IPA:Zr^{4+} = 10:50:1).

In summary we have demonstrated that the catalytic activity of zirconium terephthalates for a variety of reactions can be enhanced by adding trifluoroacetic acid in the synthesis. Trifluoroacetate groups replace part of the terephthalate linkers in the material, creating extra Lewis acid sites and a more open material. This approach can be highly valuable in exploiting the full potential of MOFs as catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis procedures, experimental methods, physical characterization, and computational procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) In this case, the proposed formula is $[Zr_6(OH)_2O_6](BDC)_5]$; charge balance around the cluster is achieved by partical replacement of OH^- ions by O^{2-} anions. Note that analogous hexanuclear Zr_6 clusters have been described as Zr_6O_8,[18] $Zr_6(OH)_4O_4$,[13,14] or even $Zr_6(OH)_8$,[19] depending on the number of linker molecules bound.

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(20) The removal of TFA was also followed by monitoring the IR spectra of the gases released during the heating of the sample from 200 to 320 °C, which showed that, besides desorption of intact CF_3COOH, the compound may also be decomposed with splitting of the C−C bond.