An amino-modified Zr-terephthalate metal–organic framework as an acid–base catalyst for cross-aldol condensation[†]

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After controlled pretreatment, some Zr-terephthalate metalorganic frameworks are highly selective catalysts for the crossaldol condensation between benzaldehyde and heptanal. The proximity of Lewis acid and base sites in the amino-functionalized UiO-66(NH₂) material further raises the reaction yields.

Metal-organic frameworks have drawn a lot of attention because of their tunable composition and structural diversity combined with a high porosity.¹ Many applications have been studied so far. Among these, gas storage and separation processes have been investigated most intensively.² Catalysis with MOFs is a much less studied field, partly because of the lower stability of MOFs in comparison to e.g. zeolites, or because of the lack of accessible active sites.³ Several strategies have been followed to introduce catalytic activity within the structure, e.g. use of functionalized ligands,⁴ post-treatment of the materials,⁵ introduction of nanosized metallic clusters,⁶ or use of the MOFs as supports for organometallic complexes or polyoxometallates.⁷ The use of the true lattice active sites of MOFs for catalysis has only been described for a limited number of structural metal ions, including Cr,8 Fe,9 Cu,10 Zn,¹¹ Mn,¹² Sc,¹³ etc.

Recently a few highly stable MOFs were synthesized using less common metals like Ti and Zr.^{14,15} The stability of these MOFs is an incentive for their use in catalysis. For instance UiO-66 [Zr₆O₄(OH)₄(O₂C-C₆H₄-CO₂)₆] (UiO for University of Oslo) shows high thermal stability due to the presence of the Zr₆O₄(OH)₄ inorganic building blocks.¹⁵ The triangular faces of the Zr₆-octahedron in this structure are alternatively capped with μ_3 -O and μ_3 -OH groups. These building units are bound to 12 other inorganic subunits through terephthalate ligands. This results in a square-antiprismatic coordination of each Zr atom with eight oxygen atoms, of which four derive from carboxylates, and four from μ_3 -O and μ_3 -OH groups. The framework itself comprises tetrahedral and octahedral cages, in a 2:1 ratio, of free dimensions close to 8 and 11 Å respectively. Access to the cages is provided by triangular windows with a free diameter of close to 6 Å. We here disclose that in the amino-substituted analogue UiO-66(NH₂), the cooperative action between the framework Lewis sites and ligand base groups results in high yields for the cross-aldol reaction.

UiO-66 was readily prepared under solvothermal conditions at 393 K in dimethylformamide starting from ZrCl₄ and terephthalic acid; the material displayed an X-ray powder diffraction (XRPD) pattern identical to the reported one.¹⁵ Simple replacement of terephthalic acid by 2-aminoterephthalic acid in the procedure leads to highly crystalline UiO-66(NH₂) in the same conditions of solvent and temperature, even if the synthesis duration was adapted because of the accelerating effect of the amine group on the crystallization. UiO-66 exhibits a rigid structure, and we expect the diffraction pattern of UiO-66(NH₂) to be highly similar to that of the nonsubstituted material, which was also confirmed by measuring the XRPD.16 The measured BET surface areas, following the consistency criteria, 20 of UiO-66 and UiO-66(NH₂) are 891 m² g⁻¹ and 1206 m² g⁻¹, respectively, indicating the highly accessible surface area of both materials. Based on the SEM observations, both materials occur as small cubic crystals of ~ 100 nm.⁺ TGA confirms the high thermal stability of UiO-66, which collapses only at temperatures above 723 K, while the aminosubstituted variant is stable up to 548 K. Long-term thermal stability of UiO-66(NH₂) was confirmed in a test for 3 months at 433 K.[†] Both UiO-66 and UiO-66(NH₂) are moisture stable and as proven by thermogravimetric analysis of DMF-free samples, they exhibit a high water affinity, adsorbing, respectively, 16 and 22 wt% water in 79% relative humidity. This implies that at least a mild dehydration will be necessary before initiating reactions with adsorbed organic compounds.

The UiO-66 materials were evaluated as catalysts in the synthesis of jasminaldehyde (JA, α -*n*-amylcinnamaldehyde). This fine chemical compound is applied in perfumery for its violet scent and is commercially synthesized by the condensation of heptanal (HA) and benzaldehyde (BA) using NaOH or KOH as homogeneous basic catalysts (reaction (1) in Scheme 1).¹⁷ Sorption experiments confirmed that UiO-66 and UiO-66(NH₂) adsorb up to 25 wt% of jasminaldehyde





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from hydrocarbon solutions, proving that the pores are of sufficient dimensions.§

Results of the reactions are shown in Table 1. The samples used were either heated for a short duration at 423 K under air to remove adsorbed water or were subjected to a more severe dehydration at higher temperature under deep vacuum $(<10^{-6}$ bar for 6 h). A low heptanal to benzaldehyde ratio of 1/15 was selected to limit the production of 2-pentyl-2-nonenal by self-condensation of HA (reaction (2) in Scheme 1).

The activity strongly depends on the catalyst pretreatment. UiO-66 heated under air after 1 h gives much less conversion than the same material pretreated under deep vacuum at 573 K (entries 2 vs. 3). Also, the eventual yield at full HA conversion varies among the samples, with the best combination of high yield and high initial rate observed for UiO-66(NH₂) (entry 4).

In order to understand the effect of the pretreatments, the dehydration process was followed in situ using FTIR (Fig. 1). Self-supporting wafers of the MOFs were mounted in a heated vacuum FTIR cell, and spectra were recorded at different temperatures in order to determine the effect of the pretreatment on the μ_3 -OH groups of the Zr inorganic building block. The clear ν_{O-H} stretching vibration of UiO-66 gradually shifts upon thermal treatment under deep vacuum, from 3673 cm^{-1} at 298 K, till 3665 cm⁻¹ at 523 K, until it completely disappears at 573 K. As proposed by Lillerud et al.,¹⁵ this corresponds to the transformation of the Zr₆O₄(OH)₄ unit to the Zr_6O_6 core, with potential access to one open coordination site per Zr atom. The creation of these Lewis acid sites readily explains the enhanced catalytic activity of UiO-66 after dehydroxylation (Table 1, entries 2 vs. 3). Such acid functions are able to activate either heptanal or benzaldehyde, thus increasing the reaction rate. UiO-66(NH₂) presents similar spectra. Besides the strong ν_{N-H} vibrations, the ν_{O-H} is observed at 3670 cm⁻¹, albeit with a weaker intensity than in UiO-66. This might be due to the presence of intra-framework hydrogen bonds between the amino and the hydroxyl groups, as reported previously for MIL-53(NH₂),¹⁸ or to a partial dehydroxylation even at room temperature. In any case, progressive dehydroxylation of the framework is observed upon heating to 373 K and full dehydroxylation is already achieved at 473 K. Note that for both materials, rehydration fully restores the original spectra, which, together with XRD follow-up, ensures that the materials survive the pretreatments intact.

Table 1 Conversions and selectivities after 1 h of reaction, and jasminaldehyde yield at full HA conversion for the solventless reaction of BA (1.4 g) and HA (0.1 g) in the presence of 10 wt% catalyst (393 K)

	Catalyst	Conversion ^{<i>a</i>} (%)	Selectivity ^{b} (%)	Yield ^c (%)
1	_	1	_	_
2	$UiO-66^d$	30	82	85
3	UiO-66 ^e	42	81	80
4	$UiO-66(NH_2)^d$	67	91	92
5	$UiO-66(NH_2)^f$	38	90	92

^{*a*} Conversion of HA after 1 h. ^{*b*} Selectivity for JA, based on HA after 1 h. ^{*c*} Yield of JA, at full HA conversion after 24 h. ^{*d*} Pretreated under air (423K). ^{*e*} Pretreated under deep vacuum at high temperatures (573 K). ^{*f*} Pretreated under deep vacuum at high temperatures (473 K).



Fig. 1 Infrared spectra of (A) UiO-66 and (B) UiO-66(NH_2), as such, or upon dehydration in deep vacuum (bottom).

Two hypotheses can be forwarded to explain the reactivity of samples that were not subjected to a deep dehydroxylation pretreatment. First, the (weak) Brönsted acidity of the O–H groups may play a role. Alternatively, the temperature dependent spectra (Fig. 1) show that dehydroxylation starts at temperatures around 373 K for UiO-66, or even below 373 K for UiO-66(NH₂). As samples were dehydrated at 423 K to remove physisorbed water from the pores, and as the reaction itself takes place at 383 K, even these mild conditions are sufficient to induce partial dehydroxylation in reaction conditions. As expected, fully dehydroxylated UiO-66 is more active but the selectivity somewhat suffers from the production of the HA self-condensation product (\sim 20% of products formed), which can be explained by the presence of too many strong Lewis sites in the material.

By contrast, UiO-66(NH₂) combines high activity with high selectivity, resulting in yields that are eventually ~10% higher than for UiO-66. It was shown previously, *e.g.* for aluminophosphate materials,¹⁹ that the combination of acid and base sites results in superior performance for a cross-aldol reaction: a Lewis acid site can interact with the carbonyl group of benzaldehyde, increasing its polarization and facilitating the attack of heptanal, which is activated on a nearby base site. In UiO-66(NH₂), the Zr sites can activate benzaldehyde, while the aminogroups in close proximity can activate the methylenic group in the aliphatic aldehyde, leading to the superior selectivity reported in Table 1.

Some further reactions were undertaken to optimize the reaction for UiO-66(NH₂). Increasing the temperature to 433 K raised the yield to 90% after 1 h. Hot filtration tests proved that the catalytic activity was associated with the solid exclusively, and not with the liquid phase.[†] The cubic lattice is intact after the catalytic experiments. By gradual addition of the heptanal through a syringe pump to a mixture of benzaldehyde and

UiO-66(NH₂), the reaction yield was eventually maximized at 93%, for a moderate overall benzaldehyde/heptanal ratio of 5/1.

In conclusion we report the highly selective synthesis of jasminaldehyde using a new amino-functionalized Zr-terephthalate UiO-66 framework. The close proximity of Zr Lewis acid sites and basic aminogroups inside the cages suppresses byproduct formation and accelerates the cross-aldol reaction.

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Notes and references

‡ Synthesis of UiO-66(NH₂): 13.5 mmol ZrCl₄ (Acros), 13.5 mmol 2-aminoterephthalic acid (Sigma-Aldrich) and 13.5 mmol H₂O were dissolved in 6.7 mol *N*,*N*-dimethylformamide (Acros) at room temperature. Crystallisation was carried out in a 1 1 Schott bottle under static conditions in a preheated oven at 120 °C for 6 h. The resulting solid was filtered and repeatedly washed with DMF to remove the unreacted ligand. XRPD reflection patterns of surface samples were recorded on a STOE STADI MP in Bragg–Brentano mode (20–0 geometry; CuK α_1) using a linear position sensitive detector. SEM micrographs were recorded using a Philips XL30 FEG after coating with Au. N₂ physisorption was recorded on a Quantachrome instrument.

§ Typical condensation procedure: a mixture of 100 mg heptanal and 1400 mg benzaldehyde was injected in a vial containing 150 mg catalyst. The reaction mixture was stirred at 700 rpm and heated in an aluminium heating block (373 K–433 K). Reaction samples were filtered through a 0.45 µm filter and analyzed with a Shimadzu 2014 GC equipped with a FID detector and an apolar CP-Sil 5 CB column. The identity of the reaction products was verified by GC-MS (Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer).

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