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Engineering the Environment of a Catalytic Metal–Organic Framework by Postsynthetic Hydrophobization

Jerome Canivet, Sonia Aguado, Cecile Daniel, and David Farrusseng*^[a]

Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries. Often, however, reactions can be hindered or reaction rates limited by poisoning effects originating from moisture in the air or from the water formed during the organic transformation. Water can be adsorbed and block catalytic sites, leading to their deactivation.^[1–3] This drawback has motivated the design and engineering of catalytic materials with hydrophobic features, such as the hydrophobic outer shell of enzymes, to prevent water-induced catalyst poisoning.

Metal–organic frameworks (MOFs) represent an extensive class of porous organic–inorganic crystalline materials.^[4–11] Due to their calibrated pore size, they are regarded as new shape-selective catalysts analogous to zeolites. MOFs have already been reported to catalyze a broad range of organic transformations involving their Lewis acid nodes as well as their Brønsted acid–base properties.^[12,13] Many reports have dealt with carbon–carbon bond formation catalyzed by unmodified MOFs through reactions such as Suzuki–Miyaura cross-coupling,^[14] the Mukaiyama aldol reaction,^[15] alkylation^[16,17] or polymerization.^[18,19]

To obtain more sophisticated MOF catalysts, many research groups have examined the functionalization of these materials. The post-synthetic modification (PSM) of MOFs, an appealing route toward functionalized frameworks,^[20–24] involves chemical modification of the solid after formation of the crystalline structure, assuming that the primitive MOFs employed are sufficiently porous and robust. Post-synthetic modification can provide a wide range of isotopological structures from a single MOF by treating it as a substrate with a variety of organic reagents. The insertion of pendant groups onto or into the MOF makes it possible to add chemical functionality while retaining the MOF's overall framework. Cohen and co-workers extensively studied the covalent organic PSM of a variety of amino-functionalized MOFs.^[25–29] This strategy was used by his group and others to generate metal complexes on MOFs, creating a new class of Lewis acid catalysts.^[22,23,30] Furthermore, Cohen extended his study to the hydrophobization of amino-containing MOFs through amide coupling, in order to increase their moisture resistance.^[31] In a parallel work, Yaghi et al. also reported the functionalization of porous materials^[32] and especially the reactivity of ZIF-90 against an amine or a reducing agent.^[33]

The effect of the functionalization of a MOF by hydrophobic agents on its catalytic activity has, however, not been reported to date.

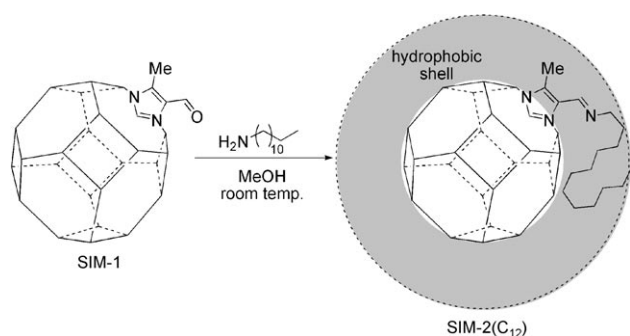
In contrast to previous studies, our methodology is based on the modification of the environment of the catalytic centers and not on the insertion of new sites onto the MOF structure. We therefore studied the ability of modified zeolitic imidazolate framework (ZIF) materials to accelerate the rate of a reaction involving water formation. We chose the Knoevenagel condensation, which is a crossed aldol condensation of a carbonyl compound with an active methylene compound leading to C=C bond formation. This reaction is widely applied in the synthesis of fine chemicals and is classically catalyzed by bases in solution.^[34] This reaction can also be catalyzed by solid bases, such as metal oxides.^[34] The water that is produced in the course of the reaction usually competes with substrates for adsorption, however, thereby acting as a poison. Porous solids such as modified SBA-1,^[35] zeolites,^[36,37] MIL-101 (TOF = 328 h⁻¹),^[38,39] IRMOF-3 (TOF = 180 h⁻¹) or MIL-53,^[40] and others^[41–43] have already been employed as active heterogeneous catalysts for the Knoevenagel reaction.

We report herein the fine tuning of hydrophobic properties of a MOF by post-synthetic modification to optimize its catalytic properties. To our knowledge, this is the first study showing that the engineering of the hydrophobic/hydrophilic environment can enhance the catalytic activity of a MOF by an order of magnitude.

Our work focused on a porous substituted imidazolate material (SIM-1, formulated C₁₀H₁₀N₄O₂Zn) discovered by our group and belonging to the class of ZIFs.^[44–46] SIM-1 is a robust material, isostructural to ZIF-8 and consisting of ZnN₄ tetrahedra linked by carboxylimidazolates. The aldehyde moiety present on the structure walls allows organic modification in the solid state, such as imine synthesis by condensation with primary amines to give the corresponding imino-functionalized SIM-2. This SIM-1 functionalization by imine condensation proceeds under mild conditions. In a typical experiment, a sample of desorbed SIM-1 (50 mg) was suspended in anhydrous methanol (5 mL) and the desired amine (1 mmol) was added under stirring. The suspension was allowed to react at room temperature for 24 h. After reaction, the solid was centrifuged and washed three times with ethanol and then dried under vacuum, providing the corresponding SIM-2 as a crystalline off-white powder. In this manner, SIM-1 was treated with the primary amines dodecylamine to give SIM-2(C₁₂) (Scheme 1). The C₁₂ aliphatic chains present at the surface of the material create a hydrophobic shell surrounding the framework.

Powder XRD analysis of the SIM-2(C₁₂) sample showed a slight loss of crystallinity despite retention of the initial structure. Notably, the porosity of the SIM materials was maintained

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Scheme 1. Post-synthetic modification of SIM-1 with dodecylamine.

throughout the modification. As expected, however, the BET surface area decreased from $470 \text{ m}^2 \text{ g}^{-1}$ for SIM-1 to $112 \text{ m}^2 \text{ g}^{-1}$ for SIM-2(C₁₂). Liquid ¹H NMR analysis after digestion in acidic DCI–D₂O–[D₆]DMSO solution showed a 22% modification according to the signal integration. The presence in the NMR spectrum of a new typical peak at 8.09 ppm, corresponding to the imino proton, confirmed the efficiency of the organic transformation. In addition, NMR spectroscopy of the fully imino-functionalized imidazole ligand alone showed no hydrolysis of the imine bond under the same conditions (see the Supporting Information). The low functionalization rate with dodecylamine can be attributed to the high steric hindrance of the alkyl chain, the C₁₂ imino moiety being nonetheless present on one fifth of the ligands.

We performed water adsorption isotherms to assess the hydrophobic feature of SIM-2(C₁₂). Comparing the data obtained with those of SIM-1, there was a dramatic effect due to the substitution with the C₁₂ chains (Figure 1). Whereas SIM-1 adsorbed water at low pressure, SIM-2(C₁₂) only adsorbed water close to the condensation point, providing evidence of the water repellence of the porous material.

The catalytic behavior of the SIM materials was then evaluated in the Knoevenagel reaction. We chose substrate combinations of two different representatives of both carbonyl and active methylene compounds that are allowed to react in a sol-

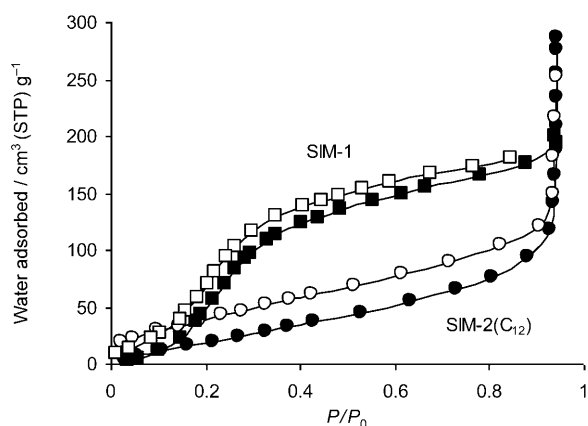
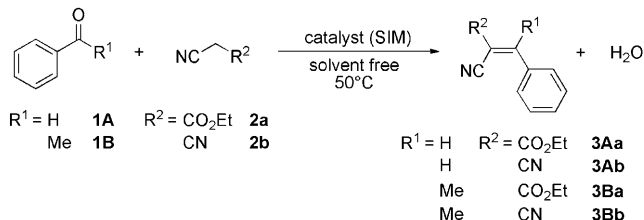


Figure 1. Water adsorption isotherms of SIM-1 (squares) and SIM-2(C₁₂) (circles) at 303 K. Closed and open symbols correspond to adsorption and desorption, respectively.

vent-free system. In a typical run (Scheme 2), either benzaldehyde (**1A**; 20 mmol) or acetophenone (**1B**; 20 mmol) reacted with either ethyl cyanoacetate (**2a**; 20 mmol) or malonitrile (**2b**; 20 mmol), with catalysis by SIM material (0.1 mol%, 6–7 mg) to give the corresponding Knoevenagel adduct **3** at 323 K.



Scheme 2. Knoevenagel condensation catalyzed by SIM materials.

According to the catalytic results (Table 1), SIM-1, ZIF-8, and SIM-2(C₁₂) were all active for Knoevenagel condensation with a catalyst loadings as low as 0.1 mol%, leading to high yields of

Table 1. Catalyst screening for Knoevenagel condensation. ^[a]					
Catalyst	R ¹	R ²	t [h]	Yield [%] ^[b]	TOF _{init} [h ⁻¹] ^[c]
none	H	COOEt	4	0	n.d.
ZIF-8	H	COOEt	0.5	40	800
SIM-1	H	COOEt	0.5	6	120
SIM-1	H	COOEt	4 ^[d]	3	n.d.
SIM-2(C ₁₂)	H	COOEt	0.5	70	1400
SIM-2(C ₁₂)	H	COOEt	4 ^[d]	80	n.d.
dodecylamine	H	COOEt	0.5	15	300
dodecylamine	H	COOEt	4 ^[d]	65	n.d.
SIM-2(C ₁₂)	H	CN	0.5	96	1920
SIM-2(C ₁₂)	CH ₃	COOEt	4	45	n.d.
SIM-2(C ₁₂)	CH ₃	CN	4	51	n.d.

[a] Reaction conditions (unless otherwise stated): **1** (20 mmol), **2**, (20 mmol), catalyst (0.02 mmol), stirred in a 10 mL glass vial under argon at 323 K; [b] determined by GC using dodecane as internal standard; [c] turnover frequencies determined after 30 min and expressed in mol₃ mol_{catalyst}⁻¹ h⁻¹; [d] reaction performed at 298 K using 1 mol% catalyst.

the compound denoted **3Aa**. The initial turnover frequencies calculated after 30 min (TOF_{init}) showed that SIM-2(C₁₂) was the most active, with a TOF_{init} of 1400 h⁻¹ for **3Aa** and 1920 h⁻¹ in the case of **3Ab**. In these conditions, we observed no formation of the Tishchenko adduct corresponding to the self-condensation of benzaldehyde. Moreover, even at room temperature, SIM-2(C₁₂) still converted **1A** and **2a** to give **3Aa** in 80% yield after four hours, whereas SIM-1 was almost inactive under the same conditions. Finally, the activity of SIM-2(C₁₂) was more than four times higher than that found for the reference molecular catalyst, dodecylamine.

SIM-2(C₁₂) was also an efficient catalyst for the reaction involving ketones, such as acetophenone **1B**, albeit with a lower activity, as already reported for zeolites.^[36,37] Figure 2 shows the time-dependent formation of ethyl cyanocinnamate, **3Aa**,

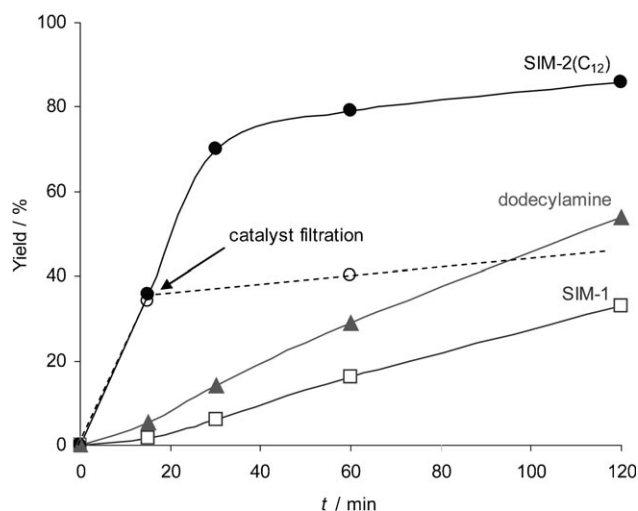


Figure 2. Time-dependent formation of **3Aa** with 0.1 mol% of SIM-1 (□), SIM-2(C₁₂) (no filtration: ●; filtration after 15 min.: ○) or dodecylamine (▲) as catalysts at 323 K.

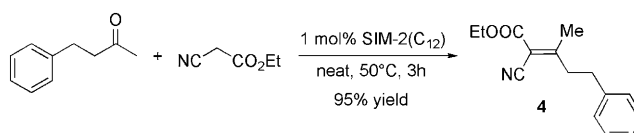
catalyzed by 0.1 mol% of SIM-1, SIM-2(C₁₂), or dodecylamine at 323 K.

The kinetic plot clearly shows that the activity of SIM-2(C₁₂) is much higher than that of its parent SIM-1 or that of dodecylamine and is not the result of the simple addition of the activities of its two components. Furthermore, in these conditions, full conversion was obtained after 12 h for all of the catalysts. Stability is a critical issue for the catalytic application of MOFs. Nevertheless, ZIF-type materials are among the most stable.^[47] To prove the stability of our new catalyst, a leaching test was performed. After 15 min, the catalyst was removed by filtration and the evolution of the product **3Aa** was followed with the same reaction conditions maintained (Figure 2, ----). No further reaction took place after the removal of the catalyst, which demonstrates the absence of leaching of active sites. After washing with ethanol and drying, SIM-2(C₁₂) was introduced in a second catalytic run under the same conditions without significant activity loss, which illustrates that it is possible to reuse the catalyst. In addition, ¹H NMR spectroscopy and PXRD analysis of SIM-2(C₁₂) were performed after catalysis and showed that the dodecylimino groups were retained by the material and that its crystallinity was preserved (see the Supporting Information). However, for real practical applications, further recycling tests would be performed.

Although the mechanism of the catalytic reaction remains unknown, we speculate that the active centers are located at the external surfaces of ZIF-8, SIM-1, and SIM-2(C₁₂) crystallites. Indeed, recent studies performed on ZIF-8 showed that crystalline defects (i.e., monocoordinated imidazoles or imidazolates) or zinc hydroxide surface species, which are Brønsted bases, are involved in acid–base catalysis.^[48,49] This hypothesis, however, cannot fully explain the differences observed between SIM-1 and SIM-2(C₁₂) in terms of catalytic activity. The enhanced kinetics can also not be attributed only to the introduction of imino basic sites. We suggest instead that the hydrophobic chains at the surface of the solid, in the vicinity of

the catalytic centers, hinder or limit water adsorption, making the centers free to adsorb the substrates.

To demonstrate the synthetic utility of the present hydrophobic SIM-2(C₁₂) catalyst, a rapid synthesis of ethyl 2-cyano-3-methyl-5-phenylpent-2-enoate (**4**) was examined (Scheme 3). Compound **4** is a precursor of citronitrile, a citrus-like odorous compound that is widely used in the cosmetic and fragrance industries. SIM-2(C₁₂) efficiently catalyzes the reaction between benzylacetone and ethyl cyanoacetate to give the Knoevenagel adduct **4** with 95% yield after three hours at 50 °C.



Scheme 3. SIM-2-catalyzed synthesis of citronitrile precursor.

In summary, we have reported herein the upgrading of a metal–organic framework catalyst by post-synthetic modification. The new catalyst generated showed a tenfold activity increase compared to its parent compounds or other MOFs. We attribute the significant acceleration of the reaction to the modification of the environment of the catalytic sites through the creation of a hydrophobic shell surrounding the structure, as found in enzymes. In principle, the same hydrophobization procedure can be applied to the isostructural ZIF-90.^[33] We believe that the development of post-synthetic functionalization routes will make it possible to achieve tailor-made materials that will bridge the gap between MOFs and enzymes.

Experimental Section

General

All reactions were carried out in anhydrous solvents and catalytic runs were performed under argon atmosphere. The initial SIM-1 was synthesized according to our previously-published method.^[44] All other reagents were commercially available and were used without further purification. NMR spectra were recorded on a Bruker 250 MHz spectrometer. The XRD measurements on the materials were carried out by powder X-ray diffraction (PXRD) using a Bruker D5005 diffractometer equipped with a secondary graphite monochromator and a scintillation counter. Water sorption was carried out on a Belsorp Max apparatus. Catalytic products were identified compared to commercial standards and activities were determined by GC analysis using an HP-5 capillary column.

Typical post-synthetic functionalization procedure

In a typical synthesis, SIM-1 powder (100 mg, ca. 0.7 mmol aldehyde) was suspended in anhydrous methanol (10 mL) and dodecylamine (390 mg, 2.1 mmol) was added. The resultant suspension was stirred at room temperature for 24 h. The solid obtained was washed with dry ethanol (3 × 10 mL) and centrifuged three times to afford the SIM-2 material as an off-white powder. SIM-2(C₁₂) was obtained with 22% functionalization yield according to NMR.

SIM-2(C₁₂): ¹H NMR (250 MHz, [D₆]DMSO, 294 K): δ = 0.77 (m, 0.93H, CH₃), 1.16 (m, 5.5H, CH₂), 1.61–1.65 (m, 0.57H, CH₂), 2.51 (s, 3H, CH₃), 3.57–3.62 (m, 0.62H, CH₂), 8.09 (s, 0.28H, CHN), 8.90 (s, 0.27H, CH), 9.20 (s, 1H, CH), 9.85 ppm (s, 1H, CHO).

NMR spectra, N₂ adsorption isotherms and PXRD patterns of SIM-1 and SIM-2(C₁₂) are available in the Supporting Information.

Typical catalytic run

SIM-2(C₁₂) (7 mg) was introduced into a 10 mL glass vial and degassed. Benzaldehyde (20 mmol; 2 mL) and ethyl cyanoacetate (20 mmol; 2.1 mL) were then added under argon and the vial was sealed. The resultant suspension was allowed to react at 323 K for 30 min. After quenching by cooling to 0 °C, the suspension was diluted and the product dissolved with Et₂O and centrifuged to remove the solid catalyst. The supernatant was analyzed by gas chromatography and the yield determined by integration of signals using dodecane as an internal standard.

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Keywords: aldol reaction · heterogeneous catalysis · hydrophobic effect · metal–organic frameworks · postsynthetic modification

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