Tuning the Catalytic Properties of UiO-66 Metal–Organic Frameworks: From Lewis to Defect-Induced Brønsted Acidity

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ABSTRACT: The Lewis/Brønsted acidity and catalytic properties of UiO-66-type metal–organic frameworks are studied in the context of tunable acid catalysts based on the presence of linker defects that create coordinatively unsaturated Zr^{4+} centers. Fourier transform infrared spectroscopy of adsorbed CO and direct pH measurements are employed to characterize hydrated and dehydrated UiO-66 containing different number of Zr^{4+} sites associated with defects. These sites can strongly polarize coordinated water molecules, which induces Brønsted acidity in the hydrated material. Upon dehydration of the solid, the coordinated water molecules are removed, and the underlying coordinatively unsaturated Zr^{4+} cations become exposed and available as Lewis acid sites. Herein we show, for various acid-catalyzed reactions, how it is possible to shift from a Brønsted acid to a Lewis acid catalyst by simply controlling the hydration degree of the solid. This control adds a new dimension to the design and engineering of MOFs for catalytic applications.

Brønsted acid catalyst

Metal–organic frameworks (MOFs) have received a great deal of attention in heterogeneous catalysis because of their high tunability of pore structure and chemical composition.^{1–5} This can be achieved by properly selecting the structural components forming the MOF (metal and organic ligands) from an almost infinite number of possibilities, and by using postsynthesis modification strategies to introduce new functionalities.^{6–8} Moreover, the crystalline nature of these compounds allows us, in principle, to predict the acid^{9,10} and basic^{11,12} properties of MOFs with theoretical calculations based on model clusters taken from the ideal crystalline network and to establish structure–activity relationships. However, in real MOFs, the regular framework is interrupted by the (un)intentional occurrence of point defects, which can change abruptly the catalytic and adsorption properties compared to those predicted for the ideal compound. Nonetheless, the presence of defects in MOF lattices does not necessarily imply a depletion of the properties of the material, but they can bring about new types of centers that can improve catalytic performance, or even introduce new functionalities that are absent in the defect-free parent solid.¹³ For instance, in the ideal lattice of zirconium-containing UiO-66-type MOFs, Zr ions are completely saturated by the organic ligands. However, Zr^{4+} coordination vacancies are created during the synthesis of UiOs associated with missing linkers. As a result, while ideal UiO-66 should not have acid properties, the real (defective) materials display the typical reactivity of a solid acid and are active in several reactions, including esterification of carboxylic acids,^{14,15} Diel–Alder condensation,¹⁶ CO_2 cycloaddition to epoxides,¹⁷ cross-aldol condensation,¹⁸ carbonyl–ene isomerization of citronellal to isopulegol,⁹ Meerwein–Ponndorf–Verley reduc-

tion of carbonyl compounds,^{19,20} etc. Moreover, the catalytic activity of defective UiOs gradually increases with the concentration of defects in the structure.^{15,19,21}

To gain further insights into the nature of these defects under different hydration conditions and their role in the observed catalytic activity, we have now rationalized the properties of various UiOs bearing different functionalities at the organic linkers and having different numbers of defects.²² Herein we will show that Zr^{4+} defects associated with missing linkers of hydrated UiOs can strongly activate water molecules, thus behaving as typical Brønsted acid catalysts. Meanwhile, these coordinated water molecules are removed upon thermal dehydration of the solid, and the underlying Zr^{4+} sites remain exposed and available as Lewis acid centers. We will thus demonstrate that it is possible to shift from a Lewis acid to a Brønsted acid catalyst by simply controlling the hydration degree of the solid, which adds a new dimension to the design and engineering of MOFs for catalytic applications (acidity on demand). This process is depicted in Scheme 1.

Suitable catalytic test reactions have been selected to evaluate the properties of defective UiOs as either Brønsted or Lewis acid solids. On the one hand, esterification of levulinic acid is used to evaluate Brønsted acidity. Indeed, the importance of Brønsted

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Scheme 1. Linker Deficiencies (Point Defects) in Hydrated and Dehydrated UiO-66 Type Compounds

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acid sites for esterification reactions has been highlighted for micro/mesoporous zeolites,²³ heteropolyacids,²⁴ sulfated oxides,²⁵ or acid-impregnated clays.²⁶ In the case of MOFs, Goesten et al.²⁷ and Jiang et al.²⁸ showed that upon treatment with sulfuric acid, chemically stable MOF structures Cr-MIL-101 or Zr-MOF-88 can be sulfated, resulting in Brønsted acid sulfate groups attached to the terephthalate linkers with remarkable catalytic activity for the esterification of carboxylic acids. On the other side of the scale, several reactions require Lewis instead of Brønsted acid centers as the catalytic active sites. Examples of such reactions are citronellal isomerization to isopulegol through an intramolecular carbonyl-ene reaction, as well as the Meerwein-Ponndorf-Verley (MPV) reduction of carbonyl compounds with secondary alcohols. Both of them can be considered as model reactions to monitor the Lewis acid site concentration, availability, and strength of a solid catalyst. Moreover, both reactions can be catalyzed by UiO-66, as well as other MOFs containing zirconium^{20,28,29} or other metal cations.^{29–31}

Previous Results. We will start the current discussion by reviewing the data available from previous studies on UiOs. Figure 1 summarizes the main results obtained to date.

The catalytic activity of UiOs for the esterification of carboxylic acids increases with the number of defects of the solid (see Figure 1a)¹⁵ and decreases significantly upon dehydration of the solid.³² Thus, adsorbed water is beneficial

for this reaction (Figure 1b). *Ab initio* calculations confirmed that the energy barriers for the esterification reaction are considerably higher for a dehydrated defect than for a hydrated acid site. A dual Lewis/Brønsted catalytic mechanism was then proposed, which is more efficient in the hydrated solid than in the dehydrated material (Figure 1c).³²

Linker defects also increase the total amount and adsorption strength of physisorbed water of the solid surface (Figure 1d).³² This was already predicted theoretically by Snurr and co-workers³³ and confirmed experimentally by Fischer and co-workers.²¹ Thus, the higher hydrophilicity of defective UiOs compared to defect-free compounds was assumed to be the major reason for the higher catalytic activity of defective UiOs. Significant differences were also observed between UiO-66 and UiO-66-NH₂ materials (i.e., a material isorecticular to UiO-66 but bearing amino groups in the terephthalate linkers); UiO-66-NH₂ samples are slightly more active for esterification than the UiO-66 with the same number of linker defects (Figure 1a). Also, the total amount of physisorbed water in UiO-66-NH₂ was higher than in UiO-66 with a similar concentration of linker defects, and water molecules were more strongly bound (Figure 1d). Therefore, the presence of amino groups favors water adsorption, in line with previous results by Walton and co-workers.³⁴ Even though our theoretical models did not predict a direct participation of the amino groups in any of the steps of the esterification reaction, their presence increases the amount of water adsorbed by the solid compared to UiO-66.

In summary, the number of linker defects, the hydration state of the solid, and the presence or absence of amino groups (or other functional groups) in the terephthalate linkers determine the environment inside the cavities of UiOs and will all have a large impact on the catalytic properties of the final material.

In line with the results noted above, it is now convenient to analyze the differential characteristics of hydrated and dehydrated UiO compounds (both UiO-66 and UiO-66-NH₂) and containing different concentrations of linker defects, with special emphasis on determining the Brønsted acidity of the

Figure 1. Most relevant conclusions extracted from previous works on UiO-66. (a) Dependency of the rate constant levulinic acid esterification with ethanol on the number of linker defects in UiO-66 (■) and UiO-66-NH₂ (○). Reprinted with permission from ref 15. Copyright 2015 Elsevier. (b) Kinetic data of levulinic acid esterification over hydrated and dehydrated UiO-66. (c) Proposed active sites on hydrated and dehydrated UiO-66. (d) Dependency of the amount of physisorbed water on the number of linker defects in UiO-66 (■) and UiO-66-NH₂ (○). (Panels b–d are reprinted from ref 32. Copyright 2017 the authors of ref 32.)

materials. We will then explore how this knowledge can assist in tuning the catalytic properties of the material to optimize its performance in specific reactions.

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Brønsted-Induced Acidity in Defective UiO-66. FTIR Spectroscopy of Adsorbed CO. Low-temperature Fourier transform infrared (FTIR) spectroscopy of adsorbed CO is a widely used technique to monitor the type (Brønsted and Lewis), concentration, and strength of the acid sites on the surface of a solid catalyst.^{35–37} To analyze the influence of the defect content on the CO adsorption properties of UiO-66, the measurements have been performed onto two samples containing either a low (2%) or a high (7%) amount of linker defects. Further information on these samples is given in the Experimental

Section. Likewise, the effect of the hydration degree of the catalyst has been addressed by selecting two thermal activation conditions: 60 or 200 °C under vacuum for 6 h. Note that thermal activation at 60 °C is enough to remove only loosely bound (physisorbed) water molecules inside the pores, but not tightly coordinated water molecules (see below).

Figure 2 shows the infrared spectra obtained before and after the adsorption of CO. Both the number of defects of the sample and the activation procedure used before CO adsorption have a large impact on the corresponding FTIR spectra. Thus, when the samples were fully dehydrated (activated at 200 °C, top and middle parts of Figure 2), the spectra before CO adsorption present mainly a single absorption band at 3674 cm⁻¹, which has been previously attributed to the O–H stretching mode of isolated hydroxyl groups at the triangular faces of the [Zr₆(OH)₄O₄] inorganic building units, i.e., μ_3 -OH groups.³⁸ Note that these μ_3 -OH groups are removed only at temperatures above 300 °C. For the sample with 7% missing linkers, additional (minor) bands are also observed at 3689, 3657, and 3610 cm⁻¹, which are assigned to O–H stretching modes of different hydroxylated species, as described in detail in ref 39 and whose in-depth discussion is beyond the scope of this work.

Upon CO adsorption, the bands at 3674 cm⁻¹ in both samples are completely eroded because of the formation of hydrogen-bonded adducts between CO and the μ_3 -OH groups of the solid. These H-bonded adducts are responsible for the new (broader) band centered at 3600 cm⁻¹ ($\Delta\nu(\text{O–H}) = -74 \text{ cm}^{-1}$), while the corresponding C–O stretching mode is observed at 2153–2154

Low defects, act. 200°C

High defects, act. 200°C

High defects, act. 60°C

Figure 2. FTIR spectra of CO adsorbed (at 77 K) on UiO-66: (top) UiO-66 with 2% of linker defects, preactivated at 200 °C before (black curve) and after (red curve) CO adsorption; (middle) UiO-66 with 7% of linker defects, preactivated at 200 °C; and (bottom) UiO-66 with 7% of linker defects, preactivated at 60 °C. The inset in the bottom-right plot compares the band at 2176 cm⁻¹ for the sample with 7% of defects preactivated at 200 and 60 °C. All spectra have been normalized to the amount of Zr in each sample.

175 cm⁻¹. These values of $\Delta\nu(\text{O}-\text{H})$ are typical of very weak acid 176 sites and are in line with previous studies on CO adsorption onto

UiO-66 materials.^{40–43} In the C–O region of the spectra, 177 besides the main band at 2154 cm⁻¹ already mentioned, an 178

Scheme 2. Main FTIR Characteristics of CO Adsorbed on UiO-66

additional absorption is observed at 2178 cm^{-1} (shifting to 2173 cm^{-1} at high CO doses) for the highly defective UiO-66 sample. This band reflects the existence of coordinatively unsaturated (*cus*) Zr^{4+} ions acting as Lewis acid sites. Note that this band is also present in the less defective sample (see inset), although with a much lower relative intensity than in the more defective material. These results indicate that the amount of Lewis acid sites in UiO-66 increases with the concentration of linker defects of the solid, as expected. We will see in the following that this has a large impact on the catalytic properties of the fully dehydrated materials (*i.e.*, activated at 200 $^{\circ}\text{C}$ under vacuum) as Lewis acid catalysts. Finally, another C–O band at 2137 cm^{-1} is observed for the highest CO doses that correspond to physisorbed CO inside the MOF pores. Scheme 2 summarizes the main species and corresponding IR band assignments.

On the other hand, the IR spectrum of a partially hydrated sample (activated at 60 $^{\circ}\text{C}$) shows significant differences compared to fully dehydrated samples. In the spectrum before CO adsorption, main IR absorptions appear now at 3674, 3630, 3575 and 3630 cm^{-1} ; the latter two are absent in the spectra of fully dehydrated samples. Adsorption of CO produces a significant (although not complete) erosion of the bands at 3674 and 3630 cm^{-1} , while new bands develop at 3603 and 3570 cm^{-1} . The fate of the band at 3575 cm^{-1} is not clear because it is overshadowed by the new bands appearing after CO adsorption. In the C–O stretching region, two IR absorption bands develop at 2150 and 2142 cm^{-1} , together with a shoulder at ~ 2135 cm^{-1} (due to physisorbed CO). Note that the $\nu(\text{CO})$ band that was observed at 2178 cm^{-1} for the sample activated at 200 $^{\circ}\text{C}$ is not present in the sample activated at 60 $^{\circ}\text{C}$ (see inset in Figure 2). This means that Lewis acid sites are barely present in partially dehydrated samples.

Referring to the spectra of samples activated at high temperature discussed above, it should be clear that the bands at 3674 and 3603 cm^{-1} can readily be attributed to isolated μ_3 -OH groups and μ_3 -OH...CO H-bonded adducts, respectively, while the corresponding C–O band of these H-bonded adducts is observed now at 2150 cm^{-1} . Once these bands are assigned, we attribute the remaining absorption bands at 3630 and 3575 cm^{-1} to the ν_3 and ν_1 O–H stretching modes of water molecules coordinated to Zr^{4+} ions, respectively. Meanwhile, the bands at 3570 and 2142 cm^{-1} formed after CO adsorption should correspond to the $\nu(\text{OH})$ and $\nu(\text{C–O})$ modes, respectively, of H-bonded adducts of coordinated water molecules with CO. This

assignment is supported by previous studies on CO adsorption onto a Cr- and Al-containing MIL-100 MOF, in which similar bands were observed and were analogously attributed to water molecules coordinated to Cr^{3+} *cus* of the material interacting with CO.^{44–46} However, there are clear differences in the type of *cus* present in these two materials, *viz.* Cr^{3+} or Al^{3+} in MIL-100 and Zr^{4+} in UiO-66. The crystalline network of MIL-100 contains “intrinsic” *cus*, *i.e.*, trinuclear $\text{M}_3(\mu_3\text{-O})$ ($\text{M} = \text{Cr}^{3+}$, Al^{3+}) units in which two of the M^{3+} ions are coordinated to labile H_2O molecules on apical positions. There is a 2:3 stoichiometric amount of coordinated water molecules and M^{3+} sites in the material. In contrast, in the ideal structure of UiO-66, the Zr^{4+} ions are (in principle) completely blocked by the carboxylate ligands. Therefore, coordination of H_2O molecules is possible only at defective positions associated with linker vacancies. Thus, the number of coordinated water molecules can vary greatly from sample to sample, depending on the number of linker defects. In this way, the higher the number of linker defects of UiO-66, the higher the amount of coordinated H_2O molecules can be expected.

Note that the coordination of a water molecule to the metal cation of the MOF increases the Brønsted acidity of this molecule; *i.e.*, the O–H bond of H_2O is weakened.⁴⁷ Therefore, we can consider a Brønsted-induced acidity of UiO-66 materials upon water coordination to Zr^{4+} at defect sites, as we will show below. Janiak and co-workers also reached a similar conclusion when studying various Cr^{3+} -containing MIL-101 materials and also attributed a Brønsted-induced acidity to the materials upon water adsorption on the Cr^{3+} *cus*.⁴⁸ More recently, Yaghi and co-workers used a combination of spectroscopic and theoretical tools and concluded that coordinated water molecules were the strongest Brønsted acid sites of sulfated MOF-808 and that the material loosed its acidity on dehydration⁴⁹ (as evidenced by the lower catalytic activity of dehydrated MOF-808- SO_4 in isobutene dimerization compared to the hydrated material). As we have shown here using FTIR spectroscopy of adsorbed CO, the amount of such Brønsted-induced acid sites in UiO-66 (responsible for the band at 3630 cm^{-1}) increases with the number of linker defects, but they are present only in partially hydrated samples. When the solid is degassed at a temperature above 150 $^{\circ}\text{C}$, coordinated water molecules are removed and the Brønsted acidity is lost, in line with the results on MOF-808- SO_4 noted above.⁴⁹ As a consequence, the Zr^{4+} ions that were formerly blocked by H_2O molecules become now accessible for

Table 1. pH Values of Stirred Suspensions of Various MOFs in Methanol^a

entry	catalyst	% missing linkers	pH
1	blank (methanol alone)		6.0
2	hydrated UiO-66	7	2.5
3	filtrate of hydrated UiO-66 ^b	7	5.8
4	dehydrated UiO-66 ^c	7	3.2
5	hydrated UiO-66	2	3.7
6	dehydrated UiO-66	2	5.8
7	hydrated UiO-66-NH ₂	8.8	1.6
8	dehydrated UiO-66-NH ₂ ^c	8.8	2.2
9	hydrated UiO-66-NO ₂	0.1	3.5
10	dehydrated UiO-66-NO ₂ ^c	0.1	4.9
11	hydrated UiO-66-HAc		5.6
12	hydrated UiO-66-SO ₃ H		3.6
13	dehydrated UiO-66-SO ₃ H		3.8

^apH of a stirred suspension of 6 mg of MOF in 24 mL of methanol, 25 °C. ^bpH of the filtrate of suspension of entry 2. ^cThe MOF was dried 6 h at 200 °C under vacuum before preparing the suspension in methanol.

consequence of water coordination to the Zr⁴⁺ sites associated with linker defects. Nonetheless, the pH measured for dehydrated UiO-66 is still lower than that of pure methanol: 3.2 and 5.8 for dehydrated UiO-66 with 7% and 2% defects, respectively (entries 4 and 6), with respect to 6.0 for pure methanol. Because adsorbed water is no longer present in these samples, the measured decrease of the pH value reflects the polarizing power of the Zr⁴⁺ sites of the MOF on the methanol molecules. Indeed, Vimont et al. showed that unsaturated Cr³⁺ ions in MIL-100 were also able to strongly adsorb and polarize a number of alcohols (including methanol), thus inducing Brønsted acid sites whose strength depends on the adsorbate.⁴⁵

To determine if this trend was also observed in other MOFs, we performed similar pH measurements on UiO-66-NH₂ and UiO-66-NO₂ samples, both in their hydrated and dehydrated forms, and the results are also reported in Table 1. As can be seen, also in this case the samples produce a more pronounced lowering of the pH for the hydrated than for the dehydrated solids. It is interesting to note that the sample UiO-66-NO₂ contains a much lower concentration of defects than the less defective UiO-66 (0.1% versus 2%, respectively), and yet the pH decrease observed with the nitro-containing MOF is slightly higher: 3.5 versus 3.7 (compare entries 5 and 9). This result reflects the electron-withdrawing effect of the nitro group in the terephthalate linker, making the Zr⁴⁺ ions in UiO-66-NO₂ more electropositive and therefore increasing their net effective charge. This translates into a higher effective polarizing power (Z^2/r ratio) of the Zr⁴⁺ ions in UiO-66-NO₂ and, thus, into a higher activation of the coordinated water molecules. This is in agreement with the observation that dehydrated UiO-66-NO₂ contains stronger Lewis acid sites than UiO-66, as revealed by FTIR spectroscopy of adsorbed 5-nonanone,¹² and also indirectly evidenced by the higher catalytic activity of this compound compared to UiO-66 in Lewis acid-catalyzed reactions.^{9,12}

To complete this picture of comparative pH measurements, we included a UiO-66 sample prepared with acetic acid as a modulator (UiO-66-HAc in Table 1). It is known that the acetic acid used in the synthesis remains strongly coordinated to the Zr⁴⁺ defective sites,¹⁹ thus blocking the sites and avoiding the induction of Brønsted acidity by water coordination. Accord-

adsorption, resulting in the creation of Lewis acid sites (evidenced by the band at 2178 cm⁻¹ upon CO adsorption). Thus, these results indicate that it should be possible to tune the acid properties of UiO-66, moving from a Brønsted-induced acid to a Lewis acid catalyst, by simply controlling the hydration degree of the material through appropriate thermal treatments. Moreover, the linker vacancies increase both the amount of Brønsted acid sites in the hydrated material and the amount of Lewis acid sites in the dehydrated material. We will show below that this can be efficiently exploited to optimize the catalytic properties of the material for reactions requiring either Brønsted or Lewis acid catalytic sites.

Another important difference between UiO-66 and Cr-MIL-100 or Cr-MIL-101 materials discussed above^{45,48} is the polarizability (or hardness) of the metal ions of the MOF. The polarizing power (Z^2/r) of the metal cation is much higher for Zr⁴⁺ than for Cr³⁺: 18.6 versus 11.9 (with r in angstroms), respectively. Indeed, Cr³⁺ is considered a moderately acidic cation (the pK_a of the metal aquo complex is 4), while Zr⁴⁺ is strongly acidic ($pK_a = -0.3$).⁵⁰ Nevertheless, the effective Brønsted acidity of the adsorbed water molecules will depend not only on the polarizing power of the metal cation present in the MOF (e.g., Zr⁴⁺ or Cr³⁺) but also on the type of ligands and coordination environment imposed by the MOF structure.

pH Measurements. The Brønsted acid properties of a material can also be evidenced by measuring the pH change of a solvent upon immersing the solid inside.⁵¹ These studies are usually carried out by potentiometric acid–base titrations, in which a small amount of the solid is dispersed in an aqueous solution of a suitable electrolyte, such as NaNO₃ or NaCl, and allowed to equilibrate for several hours before the measurement. In this way, Farha and co-workers used potentiometric titration to evaluate the Brønsted acid properties of a number of water stable Zr₆- and Hf₆-based MOFs, including UiOs, NU-1000, and MOF-808.⁵² For each compound, pK_a values were determined for the three typical types of protons: μ_3 -OH, M–OH₂, and M–OH (M = Zr, Hf). In the particular case of UiO-66, the pK_a values found were 3.52 ± 0.02 , 6.79 ± 0.01 , and 8.30 ± 0.02 , respectively.

Because the above potentiometric titration measurements were carried out in aqueous media, it is evident that the same method cannot be used if we want to analyze the dependence of the hydration degree of the UiO-66 materials on their acidity. As an alternative, methanol can be chosen as a solvent instead of water, following the method used in ref 48. Table 1 shows the pH values measured for stirred suspensions of various MOFs in methanol.

As can be seen in Table 1, a suspension of hydrated UiO-66 MOFs in methanol lowers the pH of the solvent, and the effect is more marked when the amount of linker defects of the MOF increases: 2.5 and 3.7 for samples containing 7% and 2% of missing linkers, respectively (compare entries 2 and 5). In agreement with previous observations,⁴⁸ when the solid is removed by filtration or centrifugation, the pH of the filtrate is virtually unchanged compared to free methanol (see entry 3), which shows that the Brønsted-induced acidity of UiO-66 is a surface effect; that is, the pH of the solvent is lowered only in the vicinity of the solid. On the other hand, fully dehydrated UiO-66 produces a much less pronounced pH decrease than hydrated MOF: 3.2 versus 2.5 (entries 2 and 4) and 3.7 versus 5.8 (entries 5 and 6) for samples with 7% and 2% defects, respectively. These results reinforce our above interpretation of the IR results and the occurrence of a Brønsted-induced acidity of UiO-66 as a

ingly, it was observed that the pH of a methanolic suspension of the sample UiO-66-HAc is very close to that of pure methanol (entry 11). Finally, we also considered a UiO-66-SO₃H sample. In this case, it was not possible to prepare this material by a two-step synthesis procedure similar to that used for the other compounds, and it was necessary to use acetic acid as a modulator to obtain a highly crystalline material. Considering the blocking effect of the acetic acid modulator, we believe that the Brønsted acidity of UiO-66-SO₃H, responsible for the observed pH lowering to 3.6, is mostly due to the sulfonic groups in the linkers rather than strongly coordinated water molecules (as in UiO-66, UiO-66-NH₂, and UiO-66-NO₂). In agreement with this assumption, we observed practically no variations of the pH when UiO-66-SO₃H was fully dehydrated (entries 12 and 13).

UiO-66 as a Brønsted-Induced Acid Catalyst: Esterification of Carboxylic Acids. In light of the Brønsted-induced acidity of UiO-66 type MOFs discussed above, we have now reexamined the esterification of levulinic acid with ethanol as a model reaction to investigate in more detail the effect of both the number of linker defects and degree of hydration of the MOFs on their catalytic performance.

As we have discussed above, as the amount of linker defects in UiO-66 increases, the catalytic activity of the material for the esterification of LA also increases, following a clear linear trend (see Figure 1a).¹⁵ Moreover, it is also observed that the dehydration of the samples by thermal treatment at 150 °C (see Figure 1b) brings about a definite decrease in the catalytic activity of UiO-66 samples.³²

Therefore, it is evident that there is a clear interdependence of the number of linker defects and the hydration degree of the sample on one side and the measured pH in methanol and catalytic activity for esterification (*k*) on the other side. This correlation can be easily evidenced by plotting the logarithm of the rate constant of esterification, log *k*, versus the pH measured upon dispersing the catalyst in methanol, as shown in Figure 3. In this plot, we have included all the MOF samples studied, as well as other Zr- and Hf-containing DUT-67 compounds²⁹ and other reference acid catalysts, *viz.*, *para*-toluene sulfonic acid (*p*-TSA) and Amberlyst-15. The strong correlation between the reaction rate constant and the drop of the pH of methanol produced by the catalyst lend support to the hypothesis that the Brønsted-induced acid sites of the MOF are the most likely active sites for the esterification of LA. Meanwhile, the participation of Lewis acid sites of the solid (if any) must be very limited for this typical Brønsted acid catalytic reaction.

In line with the above results, it has been described that interlamellar water molecules coordinated to aluminum ions of Al-exchanged montmorillonite (Al-Mont) provide strong Brønsted acid sites to catalyze the esterification of phenylacetic acid with *p*-cresol, while the parent Na-exchanged montmorillonite was not acidic (and therefore catalytically inactive) because of the low polarizing power of Na⁺ as compared to Al³⁺ cations.⁵³ Thus, 67% conversion was attained over hydrated Al-Mont (solid dried at 100 °C), while the catalytic activity almost halved (36% conversion) when the solid was dried at 200 °C, and it was completely lost when dried at 400 °C. Therefore, the catalytic activity of the clay mirrored the hydration degree of the solid, similar to what we have observed here for Zr UiO-66-type MOFs.

Taking together all the results discussed above, it can be concluded that dehydration of the UiO-66 samples produces a desorption of water molecules strongly coordinated to defective

Figure 3. Logarithmic plot of the reaction rate constant of LA esterification (log *k*) versus the pH of a methanol dispersion of various catalysts, as indicated: *para*-toluene sulfonic acid (▲); Amberlyst-15 (▶); UiO-66-NO₂ (▼); UiO-66-HAc (◀); UiO-66-SO₃H (□); various Zr- and Hf-DUT-67 (◇). Samples of UiO-66 (■) and UiO-66-NH₂ (○) are numbered as follows: (1) Hydrated UiO-66 (7% of defects); (2) dehydrated UiO-66 (7% of defects); (3) hydrated UiO-66 (2% of defects); (4) dehydrated UiO-66 (2% of defects); (5) hydrated UiO-66-NH₂ (8.8% of defects); (6) dehydrated UiO-66-NH₂ (8.8% of defects).

Zr⁴⁺, as evidenced by the disappearance (see Figure 2) of the IR absorption band at 3670 cm⁻¹. As a result, the Brønsted induced acidity of the MOF is lost, and therefore, the pH drop of methanol upon dispersing the dehydrated solid is less pronounced (see Table 1) than in the case of the hydrated sample. In turn, dehydration and loss of the Brønsted-induced acidity cause a decrease in the catalytic activity of the MOF for the esterification of LA. These effects are more pronounced for the samples containing a higher concentration of missing linker defects.

UiO-66 as a Lewis Acid: Citronellal Isomerization and Meerwein–Ponndorf–Verley Reduction of Cyclohexanone. Isomerization of citronellal (1) produces a mixture of isopulegol diastereoisomers, namely, isopulegol, neo-isopulegol, iso-isopulegol, and neoiso-isopulegol (2–5, Scheme 3). One of these products, isopulegol (2), can be further converted into the industrially relevant product menthol through hydrogenation of the terminal C=C bond. When a Lewis acid catalyst is used for the isomerization reaction, high selectivities are usually obtained to the desired isopulegol. However, with Brønsted acid catalysts, isopulegol is still the major product of this reaction, but it is obtained with significantly lower diastereoselectivities. This trend was nicely shown by Yaghi and co-workers when studying the catalytic activity of as-prepared and sulfated MOF-808, a zirconium trimesate compound.²⁸ Those authors observed a very low activity of as-prepared MOF-808 for citronellal isomerization (8% conversion after 8 h of reaction), albeit with a high selectivity to 2 (85%). Progressive sulfation of MOF-808 increased its Brønsted acidity and accelerated the conversion rate of citronellal (98% conversion after 1.5 h for the most sulfated compound), but the selectivity to 2 dropped progressively down to 55%, reflecting the increased participation of the newly introduced Brønsted acid sites in the catalytic conversion of citronellal.

Scheme 3. Isomerization of Citronellal to Isopulegol

Figure 4. (a) Time–conversion plots of citronellal (1) over hydrated (O) and dehydrated (■) UiO-66 (7% defects). Panels b and c show citronellal conversion (■) and yields to isopulegol 2 (O) and other isopulegols 3–5 (*) for hydrated (b) and dehydrated (c) UiO-66.

To study the relative participation of Lewis and Brønsted acid sites in UiO-66, we have performed the citronellal isomerization onto hydrated and dehydrated UiO-66 containing 7% linker defects. The results are shown in Figure 4.

As it is shown in Figure 4a, dehydrated UiO-66 shows a significantly higher activity for citronellal isomerization than the hydrated solid: the calculated kinetic rate constants are 0.076 and 0.360 h^{−1} for hydrated and dehydrated UiO-66, respectively (an almost 5-fold increase). This is the exact opposite result that was found for LA esterification, for which dehydration of UiO-66 brings about a decrease of the catalytic activity. As noted above, FTIR spectroscopy of adsorbed CO reveals that hydrated UiO-66 has mainly Brønsted acid sites and virtually no Lewis acid sites (see Figure 2). Therefore, the lower activity of hydrated versus dehydrated UiO-66 indicates that citronellal isomerization is more effectively catalyzed by Lewis acid centers than by Brønsted sites. This is confirmed by the observed diastereoselectivity to isopulegol 2, which increases from 75% to 86% upon dehydration, reflecting a preferential participation of Lewis acid sites for this reaction. The participation of zirconium Lewis acid sites of UiO-66 in citronellal isomerization was recently rationalized using first-principles kinetic calculations by van Speybroeck and co-workers.⁹ Such coordinatively unsaturated Zr sites would be present at defect positions. As expected, the activity increased with the number of linker defects present

in the solid catalyst.¹⁹ Note that in hydrated UiO-66, the interaction between citronellal and the zirconium sites of UiO-66 is hindered by the presence of strongly bound water molecules, in such a way that a competition is established between both compounds to coordinate to Zr⁴⁺ centers, resulting in a slowdown of the reaction.

Another reaction that is preferentially catalyzed by Lewis over Brønsted acid sites is the MPV reduction of ketones with secondary alcohols. Indeed, it is generally accepted that this reaction proceeds through a transition state in which the ketone and the alcohol are simultaneously adsorbed onto the coordinatively unsaturated metal sites of the catalyst (acting as a Lewis acid center) and forming a six-membered cyclic structure, as shown in Scheme 4.⁵⁴ Then, a direct hydrogen transfer takes place from the alcohol to the ketone.

We then carried out the MPV reduction of cyclohexanone using isopropanol as the secondary alcohol and using as a catalyst either hydrated or dehydrated UiO-66 containing 7% linker defects. The results are shown in Figure 5.

The hydration degree of UiO-66 is a key factor governing the catalytic properties of UiO-66.

Scheme 4. Six-Membered Cyclic Transition State for the MPV Reduction of Cyclohexanone with Isopropyl Alcohol over UiO-66, Involving the Participation of Zr^{4+} Lewis Acid Sites

Figure 5. Time–conversion plots of cyclohexanone over hydrated (○) and dehydrated (■) UiO-66 (7% defects).

Brønsted acid sites (esterification of levulinic acid) or Lewis acid sites (citronellal isomerization and MPV reduction of cyclohexanone). We have shown that thermal pretreatments of the solid under suitable conditions provide a very simple means for controlling the nature of the active sites, shifting the properties of the material from a Brønsted-induced acidity to Lewis acidity. We have shown that this introduces a new dimension in the catalyst engineering that allows us to tune and optimize the performance of the MOF depending on whether the reaction in which it is going to be applied requires Lewis or Brønsted acid sites. To date, this has already been demonstrated for various reactions, including esterification, carbonyl-ene isomerization, and MPV reactions over UiO-66 (this work and ref 32); acetalization of aldehydes over functionalized MIL-101(Cr);⁴⁸ and the dimerization of isobutene over sulfated MOF-808,⁴⁹ to name a few examples.

EXPERIMENTAL SECTION

Synthesis of the MOFs. Different batches of UiO-66 were prepared by the nonmodulated synthesis described by Kandiah et al.²² For this, 750 mg of ZrCl_4 and 740 mg of terephthalic acid (UiO-66), or 800 mg of aminoterephthalic acid (UiO-66- NH_2), or 940 mg of nitroterephthalic acid (UiO-66- NO_2) were dissolved in 90 mL of *N,N*-dimethylformamide (DMF) inside a closed round-bottom flask and kept at 80 °C for 12 h without stirring, followed by 24 h at 100 °C. The solid thus formed was recovered by centrifugation, washed with fresh DMF (2×10 mL), and finally soaked in dichloromethane for 3 h. The crystallinity of all compounds was confirmed by X-ray diffraction (Phillips X'Pert, Cu $K\alpha$ radiation). The number of defects in each sample (see Table 1) was determined by thermogravimetric analysis (Mettler Toledo TGA/SDTA851e, heating rate 10 °C min^{-1} under an air flow), following the method of Valenzano et al.³⁸ The corresponding TGA curves, weight losses, and determined compositions of these samples are shown in Figure S1 in the Supporting Information.

Additional batches of UiO-66 and UiO-66 functionalized with sulfonic groups were prepared using a modulated synthesis with acetic acid (samples UiO-66-HAc and UiO-66- SO_3H), following the procedure reported in ref 19. Thus, equimolar mixtures of ZrCl_4 (3 mmol), the organic ligand (terephthalic or sulfoterephthalic acid), and 10 equiv of acetic acid were dissolved in DMF (30 mL). The mixture was heated at 120 °C for 21 h, and the powders were collected by centrifugation, washed with fresh DMF (2×10 mL), and finally soaked in dichloromethane for 3 h. The crystallinity of all compounds was also confirmed by X-ray diffraction.

All Zr- and Hf-DUT-67 and acid-treated materials mentioned in the text are the same compounds described in ref 29. Finally, the Amberlyst-15 catalyst used was a commercial sample from Sigma-Aldrich.

FTIR Spectroscopy. The acidity of the UiO-66 type compounds was evaluated using FTIR spectroscopy of adsorbed CO at liquid-nitrogen temperature. IR measurements were performed on a Nicolet iS10 FTIR spectrometer at a resolution of 4 cm^{-1} . The solids were prepared in the form of thin self-supported wafers of ca. 10 mg cm^{-2} and activated at either 60 or 200 °C overnight under vacuum (10^{-3} mbar).

pH Measurements. The method used in this work was the same as that reported in ref 48. Briefly, 6 mg of the MOF (either as-prepared or dehydrated) was dispersed in 24 mL of methanol and kept under stirring for 3 h at room temperature before pH

As was also the case of citronellal isomerization, dehydration of UiO-66 produces a significant increase of the catalytic activity, passing from a kinetic rate constant of 0.147 h^{-1} for the hydrated solid to 0.516 h^{-1} for the dehydrated material, representing a 3.5-fold increase. In line with previous results, the catalytic data for this reaction lend support to the role of the Lewis acid sites associated with linker defects in dehydrated UiO-66 as the main catalytic centers for the MPV reaction. Indeed, we have recently shown that the catalytic activity of various zirconium MOFs in the MPV reduction of cyclohexanone increases in the order MOF-808 > DUT-67 > UiO-66, reflecting the increasing availability of the Zr^{4+} sites as the coordination of the inorganic building units decreases from 12 (UiO-66), to 8 (DUT-67), and to 6 (MOF-808).²⁰ Similar results have been reported for the MPV reduction of furfural to furfuryl alcohol.⁵⁵

Concluding Remarks. Herein we have shown that the hydration degree of UiO-66 is a key factor governing the catalytic properties of UiO-66, in line with previous observations from our lab and by other groups. We have shown that thermal treatment under a vacuum at low temperature (<100 °C) removes physisorbed water molecules trapped inside the MOF pores. However, tightly bound water molecules directly coordinated to zirconium ions at defect positions are still present and require outgassing at higher temperatures (viz. 200 °C) to be completely removed. These coordinated water molecules are strongly polarized by the Zr^{4+} ions of UiO-66, resulting in the creation of strong Brønsted-induced acid sites. These sites have been revealed by both FTIR spectroscopy of adsorbed CO and direct pH measurements in methanol.

We have comparatively evaluated the catalytic properties of hydrated and dehydrated UiO-66 in reactions requiring either

measurements. The amount of MOF used was high enough so the measured pH was independent of the solid content.

Catalytic Reactions. Catalyst Activation (Dehydration). When mentioned in the text, dehydrated MOF catalysts were preactivated before running the reaction. To do so, the desired amount of fresh MOF was placed directly inside the batch reactor and thermally treated at 150 °C under a vacuum (10^{-3} mbar) overnight. To start the catalytic reaction, the preheated solvent and the reagents were directly added to the catalyst inside the batch reactor to avoid exposure to ambient moisture.

Esterification of Levulinic Acid. Levulinic acid (LA) (1 mmol) and 0.6 mL of ethanol (15 mmol) were contacted with the MOF (0.018 mmol of metal) in a batch reactor at 80 °C. The reaction was monitored by GC-MS instrument (Varian 3900) equipped with a BP20(WAX) column (15 m long, i.d. 0.32 mm) and using dodecane as an internal standard. Retention times of the products were compared with those of commercial standards for reference.

Citronellal Isomerization. The reaction was performed at 80 °C under an N_2 atmosphere. Racemic citronellal (60 μ L) and MOF (30 mg) were placed inside a round-bottom flask with 0.5 mL of cyclohexane. The reaction was followed by GC-MS instrument equipped with a 30 m long and 0.25 mm i.d. capillary column HP-5 (5% phenylmethylpolysiloxane) and using dodecane as an internal standard. Retention times were compared with those of commercial standards.

MPV Reduction of Cyclohexanone. In a typical reaction, 10 mg (0.1 mmol) of cyclohexanone was dissolved in 0.5 mL of iPrOH (ca. 6.5 equiv). The solution was added to the solid catalyst (14 mol % of metal) under nitrogen atmosphere, and the mixture was transferred into a 2 mL glass batch reactor charged with a magnetic stirrer. The reactor was closed and heated in a metal heating block to 80 °C under stirring. The reaction was followed by GC on an Agilent 7890A instrument equipped with an FID detector and a DB5 column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c00984>.

Additional thermogrammetric analysis and weight loss data (PDF)

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Notes

The authors declare no competing financial interest.

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Francesc X. Llabrés i Xamena, or Xesc for short (WoS Researcher ID 669 A-4123-2008), was born in Alaró (Mallorca). He received his PhD in 670 Chemistry in 2000 from the University of the Balearic Islands (Spain) 671 working with Prof. C. Otero in the synthesis and spectroscopic 672 characterization of zeolites. After a 2-year postdoctoral stay at the 673 University of Turin with Prof. A. Zecchina, a short stay as invited 674 researcher at Polimeri Europa (ENI) in Novara, and one year at the 675 University of Padua with Prof. G. Granozzi, he joined the group of Prof. 676 A. Corma at the ITQ in 2004 as a Ramón y Cajal Fellow. In 2010 he was 677 appointed as Tenured Scientist of the Spanish National Research 678 Council (CSIC) at the ITQ. His current research interests are in the 679 preparation of metal–organic frameworks (MOFs) and the study of 680 their applications, including heterogeneous catalysis. Among other 681 prizes and recognitions, Xesc has been distinguished with the 10th 682 Duran Farrell Award of Technological Research and the Alpha Gold 683 award of the Spanish Ceramic and Glass Society. 684

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