Size Selectivity of a Copper Metal–Organic Framework and Origin of Catalytic Activity in Epoxide Alcoholysis

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Abstract: $\{Cu(bpy)(H_2O)_2(BF_4)_2(bpy)\}$ (Cu-MOF; MOF = metal-organic framework; bpy = 4,4'-bipyridine), with a 3D-interpenetrated structure and saturated Cu coordination sites in the framework, possesses unexpectedly high activity in the ring-opening reaction of epoxides with MeOH, although the reaction rate drops remarkably with more bulky alcohols. This (apparent) size selection and the single Cu²⁺ sites in an identical environment of the crystalline matrix resemble zeolites. The real nature of active sites was investigated by attenuated total reflection infrared (ATR-IR), Raman, EPR,

Introduction

Metal–organic framework (MOF) materials are promising candidates as new heterogeneous catalysts due to their high surface area inside the pores and their tunable structure.^[1-5] An attractive feature of these solids is the presence of single-site active species in an identical environment of the crystalline matrix. The research on catalytic applications has been focused on rigid MOFs with permanent porosity and coordinatively unsaturated metal active sites that are acces-

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and UV/Vis spectroscopies. Cu-MOF has highly dynamic structural properties that respond to MeOH; its framework dimensions change from 3D to 2D by restructuring to a symmetric coordination of four bpy units to Cu. This interaction is accompanied by the partial dissolution of Cu-MOF as multi-Cu clusters, in which Cu^{2+} ions are connected with bpy ligands. Although both molecular and surface catalysis contrib-

Keywords: alcoholysis • copper • epoxides • EPR spectroscopy • metal–organic frameworks ute to the high rate of alcoholysis, the soluble oligomeric species (Cu_mbpy_n) are far more active. Finally, addition of diethyl ether to the reaction mixture induces the reconstruction of dissolved and solid Cu-MOF to the original framework structure, thereby allowing excellent recyclability of Cu-MOF as an apparent heterogeneous catalyst. In contrast, the original Cu-MOF structure is maintained upon contact with larger alcohols, such as *i*PrOH and *t*BuOH, thus leading to poor activity in epoxide ring opening.

sible to the substrate.^[4,6–10] In contrast to such "conventional" structures, less attention has been paid to MOFs that have a dynamic and flexible framework, although they have shown promising potential application in adsorption and separation.^[11–21] They could provide new opportunities in designing solid catalysts due to the dynamic structural change in response to guest molecules in a manner reminiscent of enzymes.^[22–25]

An open-pore structure within the solid catalyst, that is, the accessibility of the active sites for the substrate, is crucial to achieve high catalytic activity. In contrast to expectations, excellent catalytic performance of some nonporous MOFs has also been observed. Blake et al. developed a novel hydrogen-bond-regulated, dynamic, Cu-based MOF, {Cu(bpy)-(H₂O)₂(BF₄)₂(bpy)} (Cu-MOF; bpy=4,4'-bipyridine), which consists of two-dimensional sheets (Scheme 1).^[26] The octahedral Cu²⁺ sites are linked directly through bpy units and also through intermediate hydrogen-bonded water molecules. The sheets are connected with hydrogen bonds between an F atom of a BF₄⁻ anion and an H atom of a water molecule from the neighboring sheet. In the structure of Cu-MOF, the Cu sites are coordinatively saturated and there





Scheme 1. Representation of the *ab* plane of the Cu-MOF crystal (according to ref. [26]).

are no open pores due to sheet stacking. Nevertheless, it adsorbs CO_2 after partial removal of water molecules,^[27-29] and adsorption of small amounts of methanol and acetonitrile induces structural changes that are well observable with magic

angle spinning (MAS) NMR spectroscopy combined with EPR spectroscopy.^[30] In addition, it is a highly effective catalyst in the oxidation of trime-thylsilyl enolates to α -hydroxy ketones using molecular oxygen as oxidant.^[31,32]

We have developed an alternative and more facile synthesis method for Cu-MOF and applied it as a Lewis acid catalyst in the ring-opening reaction of epoxides with alcohols to the corresponding 1-alkoxy-2-phenylethanols with excellent recyclability.^[33] In particular, among the investigated alcohols only

methanol showed high reactivity, comparable to that of the homogeneous Cu catalyst (Figure 1).^[34-36] The strong dependence of the reaction rate on the steric bulkiness of the reactant was interpreted as an indication to the location of active sites inside the micropores of the catalyst. A further, combined catalytic and spectroscopic analysis, however, revealed that the origin of this change in reactivity is not the hindered diffusion of the bulky alcohols inside the pores, rather the substrate-induced structural changes of Cu-MOF. We present here a detailed analysis of the nature of the catalytically active sites in Cu-MOF using attenuated total reflection infrared (ATR-IR), Raman, EPR, and UV/Vis spectroscopic techniques that allowed us to rationalize the excellent catalytic activity in the methanolysis of epoxides.



Figure 1. Ring-opening of styrene oxide with alcohols with Cu-MOF (black) and the homogeneous catalyst Cu(BF₄)₂-H₂O (gray). Reaction conditions: 0.11 mmol Cu, 5 mL alcohol, 1.25 mmol styrene oxide, RT, 2 h.^[33]

Results and Discussion

Structural changes of Cu-MOF induced by alcohols: The ATR-IR spectrum of Cu-MOF showed several bands characteristic of BF_4^- , bpy, and structural water (Figure 2a). The broad, intensive bands of the BF_4^- anion were observed in the range of 950–1100 cm⁻¹. The asymmetric stretching band of the BF_4^- anion, which is symmetric in a free environment, is considerably distorted, showing several distinct sharp



Figure 2. ATR-IR spectra of a) Cu-MOF, b) Cu-MOF wetted with MeOH, c) CD₃OD, d) *i*PrOH, and e) *t*BuOH. \times marks the bands originating from the alcohols.

bands.^[37,38] This implies a highly nonsymmetric surrounding environment of the BF_4^- anion within the framework. The spectrum clearly shows the doublet features at around 1610, 1415, 1220, and 820 cm⁻¹ that originate from bpy. The first two bands represent the ring stretching modes, and the latter two are due to in-plane and out-of-plane C–H bending modes, respectively. According to DFT calculations (see the Supporting Information), the higher frequency bands of these doublet bands can be assigned to the bpy molecule directly coordinating to Cu, whereas the lower frequency bands are due to the bpy molecule bridged with H₂O through hydrogen bonding (Scheme 1). On the other hand, the region of 1800–3700 cm⁻¹ (Figure 2a) shows mainly the bands due to structural H₂O in Cu-MOF. An OH stretching band is clearly seen at 3489 cm⁻¹. The two broad bands in

the ranges $2000-3000 \text{ cm}^{-1}$ and $1700-2000 \text{ cm}^{-1}$ are derived from the hydrogen-bonding network of the framework, as revealed by comparing the diffuse reflectance IR spectra of Cu-MOF and dehydrated Cu-MOF.

Next, the structural changes induced by wetting Cu-MOF with drops of alcohols (MeOH, CD₃OD, *i*PrOH, and tBuOH) were investigated by ATR-IR spectroscopy. For the Cu-MOF wetted with iPrOH and tBuOH, the spectral features of bpy, BF₄⁻, and framework H₂O did not change (compare the spectra in Figure 2a, d, and e). It follows that iPrOH and tBuOH have virtually no influence on the structure of Cu-MOF. In contrast, a remarkable restructuring of Cu-MOF was detected upon addition of MeOH (Figure 2b), as evidenced by the merging of all doublet bands into singlet bands and by the disappearance of the two broad bands due to H_2O in 1700–3000 cm⁻¹. The latter change implies the release of structural H₂O from the Cu-MOF. Furthermore, the band features of BF_4^- anion at 950–1100 cm⁻¹ were altered considerably; the broader and less distinct bands indicate a more free and flexible environment of the anion after methanol addition. At 700-1700 cm⁻¹ the band features of the samples treated with MeOH and CD₃OD were identical except some differences due to the alcohols themselves. In the higher frequency region, new OH stretching bands at 3568 and 3351 cm⁻¹ emerged by wetting with MeOH (Figure 2b). The assignment of the OH stretching vibrations was helped by the wetting experiment using CD₃OD that revealed the corresponding bands at 2658 and 2530 cm⁻¹ (Fig-

ure 2c). It should be noted that a completely wet Cu-MOF immersed into MeOH (shown later in Figure 7a) or the Cu-MOF wetted with drops of MeOH gave identical results. The OH stretching vibrations at 3568 cm⁻¹ and its broad side band at 3351 cm⁻¹, which corresponds to the OD stretching at 2658 and 2530 cm^{-1} , likely have a similar origin: the former being isolated and the latter involved in hydrogen bonding. This implies that there are more than two kinds of MeOH species present in the wetted Cu-MOF.

Raman spectroscopy was used to gain further insight into the nature of the interaction of Cu-MOF with alcohols (Figure 3). Due to different selection rules of IR and Raman spectroscopies, the band positions of similar vibrational motions are shifted and the band intensities appear differently. It is clear from the Raman investigation that after wetting the Cu-MOF with MeOH some doublet bands merged into singlets, as observed in IR, and are shifted to higher frequencies. The most prominent band at 1288 cm⁻¹ of Cu-MOF, which was assigned to in-plane symmetric C–H stretching vibration of bpy, appeared as a singlet (Figure 3a).



Figure 3. Raman spectra of a) Cu-MOF, b) Cu-MOF wetted with MeOH, c) *i*PrOH, and d) *t*BuOH. \times marks the bands originating from the alcohols.

This vibration is the counterpart of the band that appeared as a doublet in the IR spectrum at 1227 and 1219 cm⁻¹ (Figure 2a). However, formation of the singlet in the Raman spectrum may only be apparent and caused by the significantly lower resolution of the Raman spectrum (4–8 cm⁻¹) compared to the resolution of the IR spectrum (1 cm⁻¹). Similar to the observations by IR spectroscopy (Figure 2), there was neither band shift nor intensity change after addition of *i*PrOH and *t*BuOH (Figure 3c, d). This is a confirmation that the size of the alcohol substrate plays a key role in the restructuring of Cu-MOF.

An important feature of the Cu-MOF is that the structural change induced by MeOH is reversible. Figures 4 and 5



Figure 4. ATR-IR spectra of Cu-MOF and CD_3OD -wetted Cu-MOF in air with elapsed exposure time from a) to d).



Figure 5. Raman spectra of Cu-MOF and MeOH-wetted Cu-MOF in air with elapsed exposure time from a) to c).

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show the evolution of the ATR-IR and Raman spectra during air exposure of Cu-MOF wetted with CD₃OD and MeOH, respectively. The use of CD₃OD was necessary to avoid the signal overlapping in the OH stretching region. The alcohol evaporated with time and the spectral features, such as doublets, were gradually recovered. The regeneration of the original Cu-MOF structure is clearly proven by these two series of experiments. Evolution of the spectra in the OH stretching region (Figure 4a-d) indicates that the structural H₂O, removed by wetting with MeOH, gradually returned to the original positions and the specific structural hydrogen bonds between H₂O and bpy were re-formed. The band characteristics of BF₄⁻ in the original Cu-MOF were also recovered with time as methanol evaporated.

Probable structure of Cu-MOF wetted by methanol: An intriguing question is the structure of the methanol-wetted Cu-MOF. There are two types of bpy ligands present in the original framework structure. They appear as distinct double bands in the IR and Raman spectra; one ligand is directly coordinated in an octahedral Cu^{II} site and the other one is connected to Cu^{II} through hydrogen bonding to water (Scheme 1). Wetting the Cu-MOF with methanol resulted in the merging of the doublet bpy bands to singlets in both the IR and Raman spectra, thereby indicating that all bpy units become structurally identical. Other important elements of the restructuring are the release of structural water, a lessspecific free environment of BF_4^- , and at least two different kinds of methanol species in the wetted Cu-MOF. Two possible structures may be envisaged based on the singlet nature of the bpy bands: 1) Complete breakage of Cu-N-(bpy) bonds, coordination of methanol to the Cu^{II} center, and stabilization of the released bpy by methanol, and 2) removal of H_2O and BF_4^- by their strong interaction with methanol and coordination of bpy to Cu, thereby yielding four identically coordinated bpy units at the equatorial Cu sites (Figure 6).

The first scenario explains the merging of the bpy bands but fails to account for the band positions of bpy upon wetting with methanol. The resulting bpy-ring stretching vibra-

tion appears at around 1614 cm⁻¹, whereas the band corresponding to bpy dissolved in MeOH appears at a significantly lower frequency, at 1599 cm⁻¹, at which bpy presumably interacts with methanol through hydrogen bonding as shown later (Figure 7c). Moreover, the release of bpy from the Cu^{II} coordination sites would destroy the Cu-MOF framework completely and lead to significant dissolution of Cu-MOF. Upon wetting with methanol, the color of Cu-MOF changed from blue to purple without any sign of dissolution of the solid material, thus ruling out the possibility of the first scenario.

In contrast, the second assumption explains the experimental observations and spectral changes well. The four bpy coordination at the equatorial Cu^{II} sites can form a stable 2D network, as illustrated in Figure 6. In this structure the ligand arrangement at the Cu^{II} center is highly symmetric and the bpy molecules would appear in the spectrum as single bands. The absence of free bpy dissolved in methanol (as shown later in Figure 7c), also supports the symmetric coordination without altering the Cu/bpy ratio. It leads us to conclude that upon wetting, methanol occupies the sites that are available in the original framework for water and BF_4^{-} . We assume that a mixture of BF_4^- , water, and methanol is present between the 2D sheets and the BF₄⁻ anions are located near the Cu^{II} centers due to the Coulomb interactions. The mixture likely behaves as a "solution" between the 2D sheets, which can interpret the environment of BF_4^- without specific intermolecular interactions upon addition of MeOH as observed by IR spectroscopy. In this reconstructed framework, methanol is present as a ligand coordinating to the Cu^{II} center and also in the "solution" between the 2D sheets. In the IR spectra, the various methanol molecules that are located in the "solution" phase and interact with BF₄⁻, bpy, or another methanol molecule may be further distinguished.

The nature of active sites in the alcoholysis of epoxides: The IR and Raman spectroscopy investigations revealed a dynamic and reversible structural change of Cu-MOF upon interaction with liquid methanol. In contrast, Cu-MOF pre-





served its original structure in the presence of the more bulky alcohols, iPrOH and tBuOH. Since the BET surface area of Cu-MOF used in the present and former^[33] studies is relatively low (16.7 $m^2 g^{-1}$), the majority of the Cu^{II} active sites are hidden in the bulk of the particles. The low fraction of surface Cu^{II} sites exposed to the reactants and the absence of the more active, dissolved oligomeric species may explain the low catalytic activity of Cu-MOF in epoxide ring-opening *i*PrOH and tBuOH with

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(Figure 1), and also with benzyl alcohol,^[33] compared to the activity of the homogeneous reference catalyst. To confirm the heterogeneity of the reaction, in a control experiment we stopped the reaction after 15 min, removed the solid part, and determined the Cu content in the filtrate. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis revealed that the leaching was almost negligible: only 0.03 and 0.04 μ mol Cu^{II} was present in the filtrate when the reactions were carried out in *i*PrOH and *t*BuOH, respectively. We assume that the origin of this small amount of Cu in the filtrate is the incomplete separation of some very small particles formed during the magnetic stirring of the slurry.

In the alcoholysis of epoxides with MeOH, the closed 3D nonporous structure of Cu-MOF is transformed into the open 2D sheets structure. After restructuring to the "active" framework, the epoxide has easy access to the Cu sites in the framework, which seems to be in line with the high activity in epoxide alcoholysis, comparable to that of the homogeneous counterpart (Figure 1). In fact, a control experiment revealed that reconstruction of Cu-MOF in MeOH was accompanied with a significant dissolution of copper into the methanolic solution of the epoxide. Table 1 shows

Table 1. Methanolysis of styrene oxide.^[a]

Cu(BF₄)₂•H₂O

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Entry	Catalyst	Amount of	t [min]	Conversion
		Cu [µmoi]	լատյ	[70]
1	Cu-MOF	110	120	93
2	Cu-MOF	110	15	21
3	filtrate ^[b]	2.6	120	66
4	simulated filtrate ^[c]	1.5	120	43

[a] Reaction conditions: 5 mL MeOH, 1.25 mmol styrene oxide, RT. [b] Cu-MOF was removed from the reaction mixture after 15 min and the reaction was continued for another 105 min. [c] The simulated filtrate was prepared by stirring Cu-MOF (0.11 mmol) in MeOH (5 mL) for 2 h at room temperature and removing the solid part.

1.5

120

33

the result of the filtration test. The solid Cu-MOF was filtered off after 15 min and the reaction was continued with the filtrate for another 105 min. During this period the conversion more than tripled, which is clear evidence of metal leaching and the activity of the dissolved Cu species. Taking into account the amounts of Cu^{2+} in Cu-MOF and in the filtrate (Table 1, entries 1–3) reveals that the specific activity of the dissolved Cu complex is higher by more than an order of magnitude compared to the restructured, solid Cu-MOF.

In another control experiment, we prepared a "simulated filtrate" by stirring Cu-MOF (0.11 mmol Cu) in MeOH (5 mL) for 2 h at room temperature and filtering off the solid part. The estimated concentrations of bpy and Cu^{II} complex in the simulated filtrate determined by UV/Vis

spectroscopy and an inductively coupled plasma optical emission spectrometer (ICP-OES) were 1.86 and 0.30 mM, respectively, giving a molar ratio of bpy to Cu^{II} of about 6:1. Using the simulated filtrate for the methanolysis of styrene oxide, the conversion was considerably lower than in the filtrate obtained after styrene oxide methanolysis (Table 1, entries 3 and 4). Parallel to the lower rate, the amount of Cu dissolved by interaction with MeOH was also smaller than that leached in the presence of MeOH and the epoxide. It leads us to conclude that the presence of styrene oxide during the reaction also contributes to the leaching of copper and the formation of an active soluble catalyst.

A further comparison of the catalytic activity of the simulated filtrate with a control experiment with $Cu(BF_4)_2 \cdot H_2O$ (Table 1, entries 4 and 5) shows that the catalytic activity of Cu^{II} species in the simulated filtrate is higher than the corresponding homogeneous catalyst $Cu(BF_4)_2 \cdot H_2O$.

The nature of dissolved Cu species in MeOH was investigated with ATR-IR spectroscopy. Figure 7a shows the spec-



Figure 7. ATR-IR difference spectra of samples obtained by subtracting the solvent MeOH: a) Cu-MOF in MeOH; b) the simulated filtrate obtained by stirring Cu-MOF (0.0672 g) in MeOH (5 mL) and removing the solid part; c) 4,4'-bipyridine in MeOH (0.01 M).

trum of the solid part of Cu-MOF immersed into MeOH. The spectral features are the same as those of methanolwetted Cu-MOF (Figure 2b). In the spectrum of dissolved Cu species in the simulated filtrate, prepared in the absence of styrene oxide reactant, the two peaks at 1614 and 1600 cm⁻¹ are attributed to bpy (Figure 7b). According to the previous discussion on the Cu-MOF treated with drops of MeOH, the presence of a peak at 1614 cm⁻¹ demonstrates that a part of bpy is directly coordinated with Cu^{II}. Comparing with the spectrum of free bpy in MeOH (Figure 7c), the presence of the peaks at 1599 and 1666 cm⁻¹ indicates that there are also uncoordinated bpy molecules present in the simulated filtrate. As mentioned previously, the molar ratio of Cu to bpy in the simulated filtrate is 1:6. This value is higher than that in the Cu-MOF (1:2), thereby suggesting that a small fraction of bpy molecules in the framework of Cu-MOF were replaced by methanol.

The structure of dissolved Cu-MOF in the simulated filtrate was further studied with the EPR spectroscopic technique. The Cu²⁺ continuous wave (CW) EPR spectra of

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some reference solutions and the simulated filtrate are shown in Figure 8 and the estimates of the corresponding spectroscopic parameters are listed in Table 2. These spectra can be analyzed in terms of an axial-type EPR signal with $g_z > g_x \approx g_y$. The lower field part of such a spectrum consists



Figure 8. CW EPR spectra of samples in MeOH at 15 K measured with microwave attenuation of 42 dB (a–e) and 6 dB (f): a) $Cu(BF_{4})_2$; b) $Cu(BF_{4})_2$ /bpy=1:1; c) $Cu(BF_{4})_2$ /bpy=1:2; d) $Cu(BF_{4})_2$ /bpy=1:4; e) the simulated filtrate; f) the simulated filtrate measured with high microwave power.

Table 2. The spectroscopic parameters of different species as determined from the experimental EPR spectra of the reference solutions of $Cu-(BF_4)_2$ with and without 4,4'-bipyridine in methanol, as well as of the simulated filtrate sample.

Species	g_z	A_z [MHz]	$g_z, g_y^{[a]}$
complex I	2.439 ± 0.003	347 ± 10	2.09 ± 0.005
complex II	2.38 ± 0.005	428 ± 10	-
complex III	2.32 ± 0.005	$448\pm\!15$	-
complex IV	2.18 ± 0.007	_	2.056 ± 0.003

[a] Only the average value of $\frac{1}{2}(g_x+g_y)$ is reported.

of a quartet of lines due to a hyperfine interaction with the nuclear magnetic moment of Cu (nuclear spin (I)=3/2 both for the ⁶³Cu and ⁶⁵Cu isotope) centered at the *g*-value position $g=g_z$ and split by the value of the *z* component of the Cu-hyperfine tensor A_z . The two values, g_z and A_z , are known to be sensitive to the type and number of ligands.^[39] This provides a useful tool to distinguish between different types of complexes present in the solution.

The EPR signal of the first reference solution (without byy) exhibits only one type of complex (complex I, Figure 8a). The higher field part of the spectrum has a specific line shape, thus indicating a tetragonal distortion of the complex (or nonequality of the ligands in the xy plane). The hyperfine splittings due to the A_x and A_y components are not resolved. A slight difference in the value of A_z for ⁶³Cu and ⁶⁵Cu isotopes is responsible for asymmetric line shapes in the low-field quartet of lines.

For the reference solutions containing bpy, a formation of more than one type of Cu complex was observed. For the solution with 1:1 Cu/bpy molar ratio (Figure 8b), in addition to complex I (without 4,4'-bipyridine ligands) a Cu–bpy complex II is formed. In the solutions with Cu/bpy molar ratios of 1:2 and 1:4, the complex I type is not present (Figure 8c and d); instead an additional complex III type is formed. In the EPR spectra of the last two solutions, a partially resolved hyperfine structure with a splitting of approximately 1.4 mT can be seen in the higher field part of the spectrum. This structure is attributed to the EPR signal coming from the complex III and can be interpreted as an interaction of the unpaired electron of the Cu²⁺ ion with the nitrogen (and possibly hydrogen) nuclei of bpy.

Regarding their appearance in the series and their relative contributions to the spectra of different solutions, the complex II and III types can be speculatively attributed to Cu complexes possessing 2- and 4-coordinated bpy molecules. As can be seen from Figure 8c–e, the exclusive formation of the discussed complexes cannot be safely stated because of the overlap of spectral lines. Nevertheless, the fact of the formation of the mentioned three types of Cu complexes is quite unambiguous.

All reference solutions with and without bpy exhibit very similar saturation behavior, which is common for single Cu centers. At 15 K the EPR signals from these samples can be saturated with the microwave attenuation of 36 dB and less. In contrast to this, the EPR spectrum of the simulated filtrate consists of two parts with completely different saturation behavior. One part of this spectrum essentially reproduces the EPR spectrum of the Cu/bpy 1:4 reference solution and has the same saturation properties. This part dominates if the spectrum is measured above the attenuation level of 42 dB (Figure 8e). The other part of the simulated filtrate spectrum is characterized by a very short relaxation time, so that it can only be slightly saturated with the full microwave power (0 dB attenuation). At the attenuation level of 6 dB, this part dominates as shown in Figure 8f. Additionally, no hyperfine splitting is observed in this part of the EPR spectrum. The averaging out of the Cu hyperfine splitting in the spectrum clearly implies a strong exchange between different Cu centers. As the hyperfine coupling of the Cu nucleus is measured to be of the order of 400 MHz, the exchange between Cu centers responsible for this EPR signal has to have at least the same (or larger) magnitude. Such a strong exchange interaction is only possible if distances between the interacting Cu centers do not exceed a few angstroms. This is also in line with the observed saturation behavior, since the relaxation enhancement due to stochastic dipolar interaction is a well-known phenomenon for magnetically coupled systems. Therefore, because of the absence of the Cu hyperfine structure, and supported by the saturation behavior, this additional EPR signal has to be attributed to multicopper clusters (complex IV in Table 2). The presence of these clusters is most likely responsible for the difference in catalytic activity of the simulated filtrate as compared with the homogeneous catalyst.

In summary, the excellent catalytic properties of Cu-MOF in the methanolysis of epoxides originate from the reconstruction of Cu-MOF in MeOH. The dissolved species can be ascribed as a Cu_nbpy_m cluster that is probably responsible for the high catalytic activity in epoxide ring opening.

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Recovery of Cu-MOF with diethyl ether: Recently, we have reported that in the methanolysis of epoxides with Cu-MOF the filtrate of the reaction mixture does not show further catalytic activity after adding diethyl ether and removing the solid from the reaction mixture, and this procedure allows the excellent recyclability of Cu-MOF.^[33] Here we investigated the recyclability of Cu-MOF with Raman spectroscopy. The spectra show that the solid recovered from the simulated filtrate by the addition of diethyl ether has indeed the same structure as that of the original Cu-MOF (compare Figure 9a and b). On the contrary, the solid obtained by di-



Figure 9. Raman spectra of samples: a) Cu-MOF; b) the solid obtained from addition of diethyl ether to the simulated filtrate followed by separation from the liquid by filtration; c) the solid obtained by directly evaporating MeOH from the simulated filtrate without adding diethyl ether.

rectly evaporating MeOH shows a different structure (Figure 9c), as evidenced by the peak shift (1288 to 1293 cm⁻¹) as well as the presence of new bands at 1591 and 996 cm⁻¹. The different structure in the latter case is attributed to the large bpy/Cu ratio of 6:1 in the simulated filtrate, compared to the 2:1 ratio in the Cu-MOF. These results confirm the important role of diethyl ether in the recovery of the original Cu-MOF from the reaction mixture. Diethyl ether is often used to synthesize the single crystals of metal–organic frameworks by solvent diffusion and is also used to precipitate and recycle metal complexes or organic polymers in synthetic chemistry.^[40]

Conclusion

Metal–organic frameworks continue to draw increasing attention as catalysts of various reactions. We have recently shown that Cu-MOF $\{Cu(bpy)(H_2O)_2(BF_4)_2(bpy)\}^{[26]}$ is active and highly selective in epoxide ring-opening reactions.^[33] In addition, its reactivity varies by more than 400fold with the size of the reactant alcohol. The present spectroscopic study reveals that this apparent size selection typical for crystalline microporous catalysts—is due to a dynamic restructuring of the MOF induced by the small reactant methanol. On the basis of ATR-IR, Raman, and EPR spectroscopic investigations, we propose that the methanolinduced reconstruction transforms the nonporous 3D CuMOF to 2D sheets with an open structure, and also to small amounts of soluble multicopper clusters. Predominantly the latter, in situ-formed Cu_nbpy_m clusters are responsible for the excellent catalytic activity comparable to that of Cu-(BF₄)₂. Accordingly, transformation of the epoxide is predominantly molecular catalysis, and surface catalysis on the reconstructed Cu-MOF sheets plays an inferior role. The rapid and complete re-formation of the original structure of Cu-MOF by addition of diethyl ether to the reaction mixture ensures the recovery and recyclability of Cu-MOF. The reversible reconstruction of Cu-MOF to an active, soluble catalyst and the recovery of the 3D solid framework at the end of the reaction offer the catalytic application of metalorganic frameworks possessing no open pores in the original structure.

This dynamic response is absent with the bulkier alcohols *i*PrOH and *t*BuOH and the slow transformation of the epoxide is attributed to heterogeneous catalysis on the low surface area of solid Cu-MOF.

Experimental Section

Chemicals: Hydrated Cu^{II} tetrafluoroborate (Cu: 21–22 mass%, Aldrich), 4,4'-bipyridine (>98%, Aldrich), and styrene oxide (>98%, Fluka) were used as received. Methanol (>99.8%, Fluka), isopropanol (>99.8%, Fluka), and *tert*-butanol (>99.7%, Fluka), were distilled from Mg before use.

Catalyst preparation and characterization: Cu-MOF was synthesized by deposition from aqueous ethanol, according to a published procedure.^[33] A solution of 4,4'-bipyridine (0.312 g, 2 mmol) in ethanol (2 mL) was slowly added to Cu(BF₄)₂·H₂O (0.309 g, 1 mmol) dissolved in water (8 mL) at room temperature. A blue precipitate formed gradually and the slurry was stirred for 4 h at room temperature. The solid was filtered off, washed with water and ethanol, dried in air at room temperature and in vacuum at 100 °C, and stored under Ar.

The crystalline structure^[26] was investigated with XRD using a Siemens D5000 powder diffraction system with $Cu_{K\alpha}$ radiation (45 kV and 35 mA) and Cu as the reference. A Fa Leco CHN-900 instrument was used for elemental analysis. Nitrogen sorption isotherms were measured at 77 K using a Micromeritics ASAP 2000 system. The estimated concentrations of bpy and Cu^{II} complex in solutions were determined by using a Varian UV-visible spectrometer (CARY 400) and an inductively coupled plasma optical emission spectrometer (ICP-OES; at ALAB AG, Switzerland), respectively.

ATR-IR and Raman spectroscopy: Infrared spectra of the solid samples with drops of alcohols wetted were measured using a Bruker VERTEX 70 spectrometer equipped with an attenuated total reflection infrared (ATR-IR) attachment (Harrick, MVP) and a liquid-nitrogen-cooled MCT detector at 1 cm⁻¹ resolution.

Infrared spectra of the liquid samples and the Cu-MOF immersed in MeOH were also measured using ATR-IR techniques to prevent saturated IR light absorption by the solvent. A home-built stainless-steel flow-through cell^[41] located in an ATR-IR attachment (OPTISPEC) mounted in a Bruker IFS-66/S spectrometer was used. A ZnSe crystal was used for the internal reflection element (IRE; bevel of 45°, $52 \times 20 \times 2$ mm, Crystran Ltd.) and fixed in the home-built stainless-steel flow-through cell. The liquid sample was passed through the home-built cell and spectra were recorded with a liquid-nitrogen-cooled MCT detector at 4 cm⁻¹ resolution. For the measurement of Cu-MOF immersed into MeOH, an ethanol slurry (2 mL) of Cu-MOF (20 mg) was added into the mask on the large face of ZnSe and the solvent was evaporated. Then the ZnSe

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coated with the Cu-MOF film was fixed in the cell and MeOH was passed through the cell.

Raman spectra were obtained using an Ocean Optics QE6500 spectrometer equipped with an InPhotonics fiber optics probe and 785 nm laser excitation.

EPR spectroscopy: The continuous wave (CW) EPR spectra were measured using a Bruker ElexSys spectrometer (microwave frequency 9.47 GHz, maximum power of the microwave bridge 200 mW). The spectrometer was equipped with a super-high Q resonator (ER 4122 SHQ) and a He-flow cryostat (ESR 910, Oxford Instruments). All spectra were recorded at the temperature of 15 K, with a modulation amplitude of 0.5 mT. For each sample the saturation behavior was checked in the attenuation range of 0–48 dB.

To analyze the EPR signal of the "simulated filtrate" (see the text), the following reference solutions of $Cu(BF_{4})_2$ (with and without bipyridine) in methanol were prepared: $Cu(BF_{4})_2$ and $Cu(BF_{4})_2$ /bipyridine with a molar ratio of 1:1, 1:2, and 1:4. For each of the reference solutions the Cu^{2+} concentration was 2 mM.

Ring-opening reaction of styrene oxide with alcohols: For a typical reaction, styrene oxide (1.25 mmol) and Cu-MOF (0.11 mmol) were stirred in alcohol (5 mL) at room temperature. At the end of the reaction, diethyl ether (5 mL) was added to the reaction mixture and the rapidly formed precipitate was removed by filtration. The reaction products were analyzed using an Agilent gas chromatograph equipped with a flame ionization detector and an HP-5 capillary column; nonane was used as internal standard.

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