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Copper metal–organic framework: Structure and activity in the allylic oxidation of cyclohexene with molecular oxygen

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ABSTRACT

Cu-MOF [Cu(bpy)(H_2O)$_2$(BF_4)$_2$(bpy)] (bpy: 4,4′-bipyridine) shows promising catalytic activity and high selectivity in allylic oxidation of cyclohexene with molecular oxygen as the only oxidant. Under close to ambient conditions and in the absence of solvent the selectivity in cyclohexene hydroperoxide reached 90%. The combined catalytic, spectroscopic, thermogravimetric, and electron microscopic study indicates that the reaction occurs at the surface of the latent porous framework and both bpy and water are involved in the active complex. Removal of the structural water at 100 °C in vacuum induces a crystal-to-crystal restructuring and opens the pores but eliminates the oxidation activity. Rehydration under ambient conditions in air regenerates Cu-MOF with small structural changes and each dehydration–rehydration cycle increases the oxidation activity. Not only dehydration–rehydration but also stirring the slurry during oxidation induces remarkable changes in the shape and size of the crystallites.

1. Introduction

The interest in metal–organic frameworks (MOFs) has increased exponentially in the past years due to their intriguing structural properties and potential applications in various fields including gas adsorption and storage, and catalysis [1–6]. From a catalytic point of view these materials are very attractive for application in the liquid phase since they possess single-site active species characteristic of homogenous catalysts, combined with the advantages of easy separation and recycling typical of heterogeneous catalysts. Especially for catalysis involving metal–organic ligand complexes, MOFs possess inherent advantages since no additional support is needed for the heterogenization and the organic microenvironment provided by the framework often allows the metal active sites to behave in a manner reminiscent of enzymes [7–10]. In addition, unique active sites can be created in the framework, which are difficult to be realized by other methods. Although the research in this field is relatively new, there are excellent examples on their application in a broad range of transformations, including selective oxidations [11–24].

Blake et al. [25] developed a novel Cu-MOF [Cu(bpy)-(H_2O)$_2$(BF_4)$_2$(bpy)] (bpy: 4,4′-bipyridine) with a hydrogen-bond regulated framework, consisting of two-dimensional sheets (Fig. 1a), which are connected by hydrogen-bonding between an F atom of a BF_4^{-1} anion on axial positions from a sheet and an H atom of a water molecule from the neighboring sheet. The neighboring sheets are shifted by $(a + b)/2$, and thus the nanoporous structure is blocked. Its unique structural feature is the differing role of the two bpy molecules in the sheet. One bridges Cu^{2+} ions directly, while the other, through hydrogen-bonding interactions, connects Cu^{2+} ions via intermediate water molecules. The other important characteristic is its dynamic structural change responding to external stimuli due to the extensive hydrogen bonding in the 3-D network. An example is the (imperfect) reversible structural change upon dehydration leading to an open-porous structure (Fig. 1b) [26]. Dynamic restructuring can be important also during catalysis in the liquid phase. We have found recently that the excellent catalytic activity and selectivity of Cu-MOF in the ring-opening reaction of epoxides derives from a reversible restructuring induced by the reactant methanol [27,28].

Herein, we report a new application of Cu-MOF, the selective allylic oxidation of cyclohexene under mild reaction conditions, using molecular oxygen as the only oxidant. Allylic oxidation is a synthetically useful transformation; it preserves the C=C double bond and allows further functionalization of the molecule. Various copper complexes are well-known catalysts of this transformation [29–33]. From an environmental point of view, oxidation with molecular oxygen on a solid catalyst in the absence of any solvent is desired, but there are only very few useful catalysts available [34–36]. Oxidation in the presence of a reactive solvent such as acetonitrile [37] or dimethyl formamide [38] cannot be considered as environmentally benign due to co-oxidation of the solvent. Some metal–organic frameworks and coordination polymers have been shown to be active in the oxidation of cyclohexene and other olefins using H_2O_2 or TBHP as oxidants [11,20,21,39–41].

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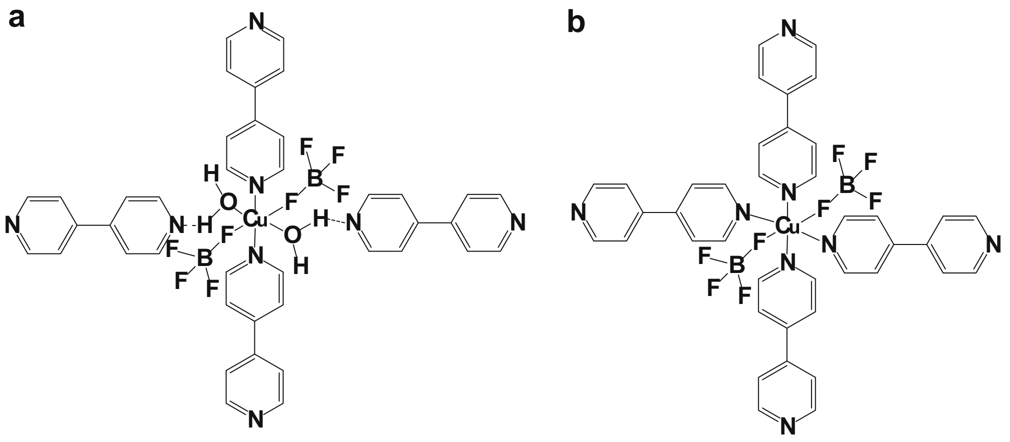


Fig. 1. Schematic illustration of the coordination of 4,4′-bipyridine (bpy) to the Cu(II) sites in an elementary unit of the planar sheets in Cu-MOF (a) and in the Cu-MOF-dehydrated (b).

2. Experimental

2.1. Materials

Hydrated Cu(II)-tetrafluoroborate (Cu: 21–22 mass%) and 4,4′-bipyridine (98%) were purchased from Aldrich. Cyclohexene (99.5%) was purchased from Fluka.

Cu(bpy)(H_2O)$_2$(BF_4)$_2$(bpy) (Cu-MOF) (Fig. 1a) was synthesized according to a published procedure [27,28]. A solution of 2 mmol 4,4′-bipyridine in 2 mL of ethanol was slowly added to 0.309 g (1 mmol) Cu(BF_4)$_2$·H_2O dissolved in 8 mL of water 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, and dried in air at room temperature. The catalyst is denoted as "Cu-MOF-as-prepared". This untreated sample was finally heat treated at 100 °C and 50 Pa for 2 h, and stored under Ar (99.996%). The catalyst is designated Cu-MOF. Note that this catalyst has been used in our earlier reports [27,28]. The dehydrated catalyst ("Cu-MOF-dehydrated", Cu(bpy)$_2$(BF_4)$_2$, Fig. 1b) was obtained by evacuating the Cu-MOF-as-prepared at 100 °C under less than 10^{-3} Pa for 2 h and then stored in Ar, due to its strongly hydrophilic character. After dehydration the sample can be rehydrated again by simply exposing the Cu-MOF-dehydrated to open air. The catalyst obtained after this complete dehydration–rehydration cycle is denoted Cu-MOF-1. The Cu-MOF-2 and Cu-MOF-3 samples were prepared analogously, applying two or three additional dehydration–rehydration cycles, respectively, after the synthesis of Cu-MOF.

Cu-MOF-lit was synthesized by vapor diffusion of diethyl ether into an aqueous acetonitrile solution of Cu(BF_4)$_2$·H_2O and 4,4′-bipyridine, according to a method described previously [25].

2.2. Catalyst characterization

The crystalline structure of the catalysts was investigated on a Siemens D5000 powder diffraction system using Cu Kα radiation (45 kV and 35 mA) and Cu as the reference.

Scanning electron microscopy (SEM) images were obtained on a Gemini 1530 (Zeiss) unit.

Inductively coupled plasma optical emission spectroscopy (ICP-OES, at ALAB AG, Switzerland) was used to check the copper content in the filtrate after reaction.

Thermogravimetric (TG and DTG) measurements combined with mass spectrometric analysis of the evolved species were performed on a Netzsch STA 409 thermoanalyzer. The composition of the gas phase was monitored by an Omni Star (Pfeiffer Vacuum) mass spectrometer, which was connected to the thermoanalyzer by a heated (ca. 200 °C) stainless steel capillary.

Infrared spectra of samples were recorded on 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 Cu-MOF immersed into cyclohexene were also measured using the ATR-IR technique. A home-built stainless steel flow-through cell [42] located in an ATR-IR attachment (OPTISPEC) mounted in a Bruker IFS-66/S spectrometer was applied. A ZnSe crystal was used for the internal reflection element (IRE, bevel of 45°, 52 × 20 × 2 mm, Crystran Ltd.).

The EPR spectra were measured with 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).

2.3. Catalytic oxidation

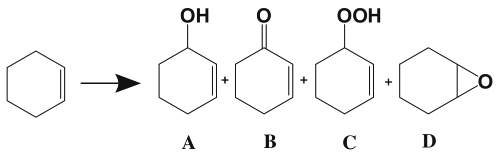
The oxidation of cyclohexene was carried out in a glass reactor equipped with a reflux condenser and an oxygen balloon. In a typical reaction 0.11 mmol of Cu-MOF (based on Cu) and 5 mL (49 mmol) of cyclohexene were stirred magnetically for 15 h at 45 °C and atmospheric pressure. The products were analyzed on an Agilent gas chromatograph equipped with a flame ionization detector and a HP-5 capillary column; tetradecane was used as internal standard. The products were identified by GC–MS, and by using authentic samples. The amounts of all four major products were determined according to a commonly used method, involving the transformation of cyclohexene hydroperoxide with PPh_3 prior to analysis; for details see Ref. [43].

3. Results

3.1. Oxidation of cyclohexene

In the oxidation of cyclohexene with oxygen under solvent-free conditions, Cu-MOF gave 2-cyclohexen-1-ol (**A**), 2-cyclohexen-1-one (**B**), cyclohexene hydroperoxide (**C**), and cyclohexene oxide (**D**) as major products. The amounts of the minor products 2,3-epoxy-cyclohexanone, phenol, and cyclohexene dimer were less than 1% for each compound. A typical example for the product distribution is shown in Table 1, entry 1. Epoxide formation was a

Table 1
Oxidation of cyclohexene. Reaction conditions: catalyst (0.11 mmol Cu); cyclohexene (5 mL); 15 h.



Entry	Catalyst	Temperature (°C)	TON[a]	Product yield (mmol)				Selectivity to **C**[b] (%)
				A	**B**	**C**	**D**	
1	Cu-MOF	45	22	0.07	0.14	2.12	0.05	89
2	No catalyst	45	0	–	–	–	–	–
3	$Cu(BF_4)_2{\cdot}H_2O$	45	0	–	–	–	–	–
4	$Cu(BF_4)_2{\cdot}H_2O$ + 4 ppy[c]	45	0	–	–	–	–	–
5	Cu-MOF	25	0	–	–	–	–	–
6	Cu-MOF	35	1.4	0.01	0.03	0.11	0	73
7	Cu-MOF	50	31	0.11	0.23	3.03	0.08	88
8	Cu-MOF (reuse)[d]	45	21	0.07	0.13	2.05	0.04	90

[a] TON = the molar amount of **A** + **B** + **C** + **D**, divided by the molar amount of catalyst.
[b] Selectivity = **C**/(**A** + **B** + **C** + **D**).
[c] Four equivalent 4-phenylpridine.
[d] Reuse of Cu-MOF after reaction in entry 1.

minor reaction and under all conditions the dominant allylic oxidation product was the hydroperoxide **C**. The high selectivity to the hydroperoxide is in good agreement with a recent observation that in a Cu- and Co-containing MOF the Cu^{2+} species were highly active in the activation of tetralin and the production of tetralinhydroperoxide, but efficient decomposition of the peroxide required Co^{2+} active sites [16].

A blank experiment (Table 1, entry 2) showed that the uncatalyzed oxidation of cyclohexene [44] was negligible under the mild conditions applied. Interestingly, the catalyst precursor $Cu(BF_4)_2{\cdot}H_2O$, alone or together with 4-phenylpyridine, was also inactive (Table 1, entries 3 and 4). Note that 4-phenylpyridine was used instead of 4,4′-bipyridine to avoid the formation of Cu-MOF.

The reaction temperature had a strong influence on the reactivity of Cu-MOF. There was no detectable conversion at 25 °C but the rate enhanced rapidly above 35 °C (Table 1, entries 1 and 5–7).

The time-dependent formation of the four major products **A–D** at 45 °C is plotted in Fig. 2a. The selectivity to the hydroperoxide **C** varied in the range 85–90% (Fig. 2b). Lower than 85% selectivity to **C** was obtained only at very low TON, at low temperature (Table 1, entry 6).

3.2. Structural effects

The last step in the synthesis of Cu-MOF is a heat treatment at 100 °C and 50 Pa, and this step induces an improvement in the oxidation activity (TON) by almost 70% (Table 2, entries 1 and 2). A possible explanation for the rate enhancement is that some impurity, probably solvent residue, diminishes the activity of the as-prepared catalyst. A characteristic feature of Cu-MOF is that its pores are blocked and thus the solvent residue (water and ethanol) cannot easily be removed from the pores after synthesis. A heat treatment at about 100 °C in vacuum leads to dehydration and restructuring (Fig. 1) to an open-porous crystal [45]. Subsequently, exposure to (humid) air at room temperature regenerates the original structure with only minor deviations. Repetition of the dehydration–rehydration cycle at even lower pressure (10^{-3} Pa, Cu-MOF-1) to facilitate complete dehydration induced another 50% enhancement in activity but further cycles led to only small changes (Cu-MOF-2 and Cu-MOF-3, Table 2, entries 3–5). Importantly, the product distribution barely changed and the selectivity to cyclohexene hydroperoxide (**C**) remained in a narrow range of 87.5 ± 1.5% for all these catalyst samples.

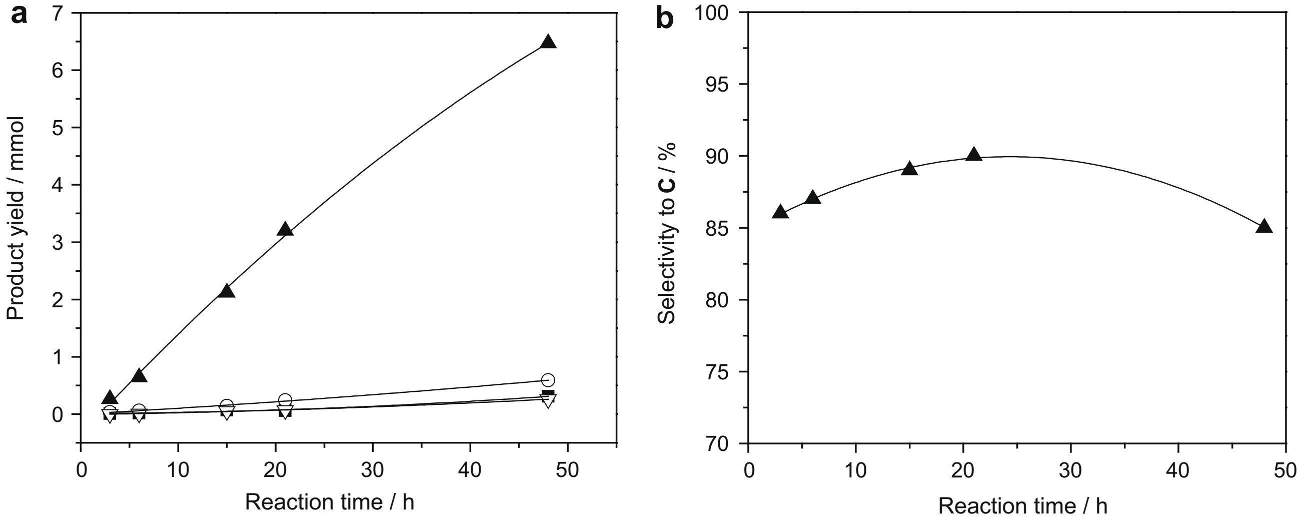
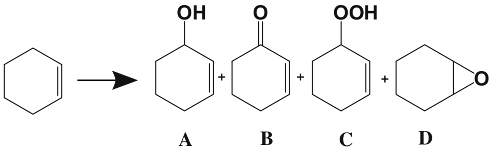


Fig. 2. Evolution of the products with reaction time at 45 °C on Cu-MOF (a), and the selectivity to **C** (b). Markers: (▲) – **C**; (○) – **B**; (▽) – **A**; (■) – **D**.

Table 2
Structural effects in the oxidation of cyclohexene. Reaction conditions: catalyst (0.11 mmol Cu); cyclohexene (5 mL); 45 °C; 15 h.



Entry	Catalyst	TON[a]	Product yield (mmol)				Selectivity to **C**[b] (%)
			A	**B**	**C**	**D**	
1	Cu-MOF-as-prepared	13	0.05	0.1	1.27	0.02	88
2	Cu-MOF[c]	22	0.07	0.14	2.12	0.05	89
3	Cu-MOF-1[d]	33	0.13	0.3	3.12	0.07	86
4	Cu-MOF-2[d]	36	0.16	0.29	3.48	0.08	87
5	Cu-MOF-3[d]	37	0.16	0.3	3.54	0.08	87
6	Cu-MOF-lit[e]	26	0.1	0.17	2.52	0.05	89
7	Cu-MOF-dehydrated	0	–	–	–	–	–

[a] TON = the molar amount of **A** + **B** + **C** + **D**, divided by the molar amount of catalyst.
[b] Selectivity = **C**/(**A** + **B** + **C** + **D**).
[c] The Cu-MOF-as-prepared was dehydrated at 100 °C and 50 Pa, then rehydrated in (humid) air.
[d] The number indicates how many additional dehydration–rehydration cycles (at 100 °C and 10^{-3} Pa) were applied to Cu-MOF.
[e] Cu-MOF synthesized according to a method described previously [25].

We applied thermogravimetry to clarify the possible presence of solvent residue in the framework. The thermogravimetric signals, the mass loss (TG) and the rate of mass loss (DTG) curves as a function of temperature, are depicted in Fig. 3. The evolution of water from Cu-MOF-as-prepared is shifted by about 5 °C to higher temperature, compared to Cu-MOF and Cu-MOF-1, while the difference between the two latter catalysts was negligible. Interestingly, the amount of evolved water was the same, 6.2 ± 0.05 mass% in all three samples investigated. The stoichiometric mass loss due to evolution of the coordinated water in $Cu(bpy)(H_2O)_2(BF_4)_2(bpy)$ is 6.15 mass%. MS signals corroborated the evolution of water ($m/z = 18$) and revealed no traces of ethanol ($m/z = 31$). Hence, the presence of solvent residue or any other volatile impurity in the as-prepared catalyst can be excluded. The probable reason for the minor shift between curve *a* and curves *b* and *c* is the partly different structure of the samples.

X-ray analysis uncovered some significant structural changes upon heat treatment of the catalyst (Fig. 4). The crystal structure of Cu-MOF-as-prepared (pattern a) is partly different from that of Cu-MOF prepared according to a literature method (pattern f). The most important deviations are represented by the additional peaks at 16.4, 16.8, 24.2, and 29.3, and the missing peak at 26.9°. The difference between the structure of the two catalysts mainly disappeared by a single dehydration of Cu-MOF-as-prepared at 100 °C under high vacuum (<10^{-3} Pa) for 2 h, followed by rehydration in (humid) air (pattern c). Evacuation at 50 Pa, applied in the synthesis of Cu-MOF, was not sufficient for this restructuring (pattern b). On the other hand, repetition of the dehydration–rehydration cycles at less than 10^{-3} Pa resulted in only minor further

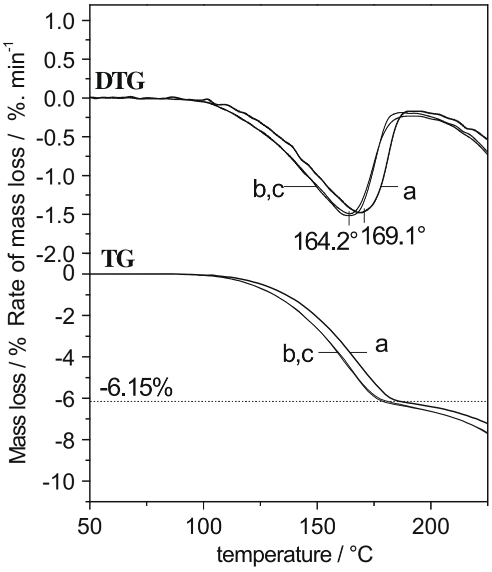


Fig. 3. Thermogravimetric analysis of Cu-MOF after various treatments: (a) Cu-MOF-as-prepared, (b) Cu-MOF: Cu-MOF-as-prepared was dehydrated at 100 °C and 50 Pa for 2 h, and then hydrated in air, and (c) Cu-MOF-1: Cu-MOF was dehydrated under less than 10^{-3} Pa at 100 °C for 2 h and then rehydrated in air. The stoichiometric mass loss due to evolution of the coordinated water from $Cu(bpy)(H_2O)_2(BF_4)_2(bpy)$ is 6.15 mass%, as indicated by the dashed line.

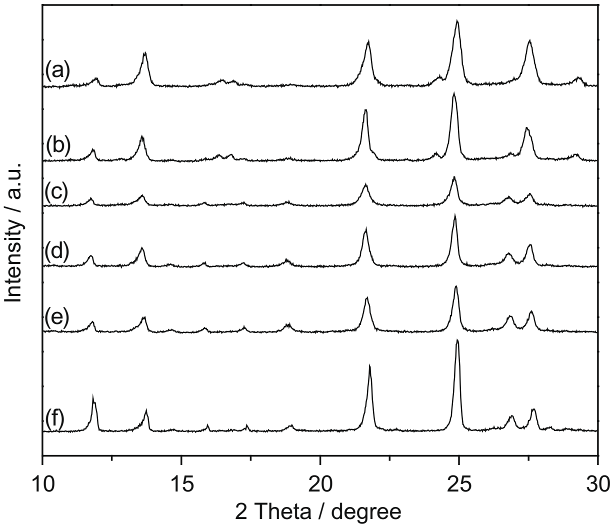


Fig. 4. XRD analysis of the catalysts after various treatments: (a) Cu-MOF-as-prepared, (b) Cu-MOF: Cu-MOF-as-prepared was dehydrated at 100 °C and 50 Pa for 2 h and then hydrated in air, (c) Cu-MOF-as-prepared was dehydrated under less than 10^{-3} Pa at 100 °C for 2 h and then exposed to air, (d) Cu-MOF-1: Cu-MOF was dehydrated under less than 10^{-3} Pa at 100 °C for 2 h and then rehydrated in air, (e) Cu-MOF-3: as Cu-MOF-1 but dehydrated and hydrated three times, and (f) Cu-MOF-lit synthesized according to Ref. [25].

changes in the diffractograms (patterns d and e). We assume that a complete dehydration of the metal–organic framework, facilitated by the very low pressure, is a necessary requirement for the structural change seen in the XRD patterns.

Scanning electron microscopy provided further information on the restructuring process. The crystal-to-crystal restructuring during evacuation and the reverse process during hydration at room temperature in air lead to a considerably different morphology, as illustrated by the example in Fig. 5a and b. It is also seen that Cu-MOF prepared according to a literature method [25] (Fig. 5c) consists of much bigger crystalline rods than Cu-MOF prepared according to our method (Fig. 5a) [27]. Fig. 5d shows, however, that during reaction the well-developed crystals are degraded in the stirred reactor to much smaller and irregularly shaped particles. The degradation during reaction was less extensive in case of Cu-MOF prepared by our method. An example with the Cu-MOF-as-prepared catalyst is shown in Fig. 5e and f. The remarkably harsh and uneven effect of stirring in the slurry reactor on the catalyst particle size and morphology is the probable explanation for the similar activities of Cu-MOF, Cu-MOF-1, and Cu-MOF-lit (Table 2), despite their different particle size and shape before use.

The XRD, thermogravimetric, and electron microscopic studies provide a plausible explanation for the catalytic results in Table 2. The original structure of Cu-MOF-as-prepared is poorly active in

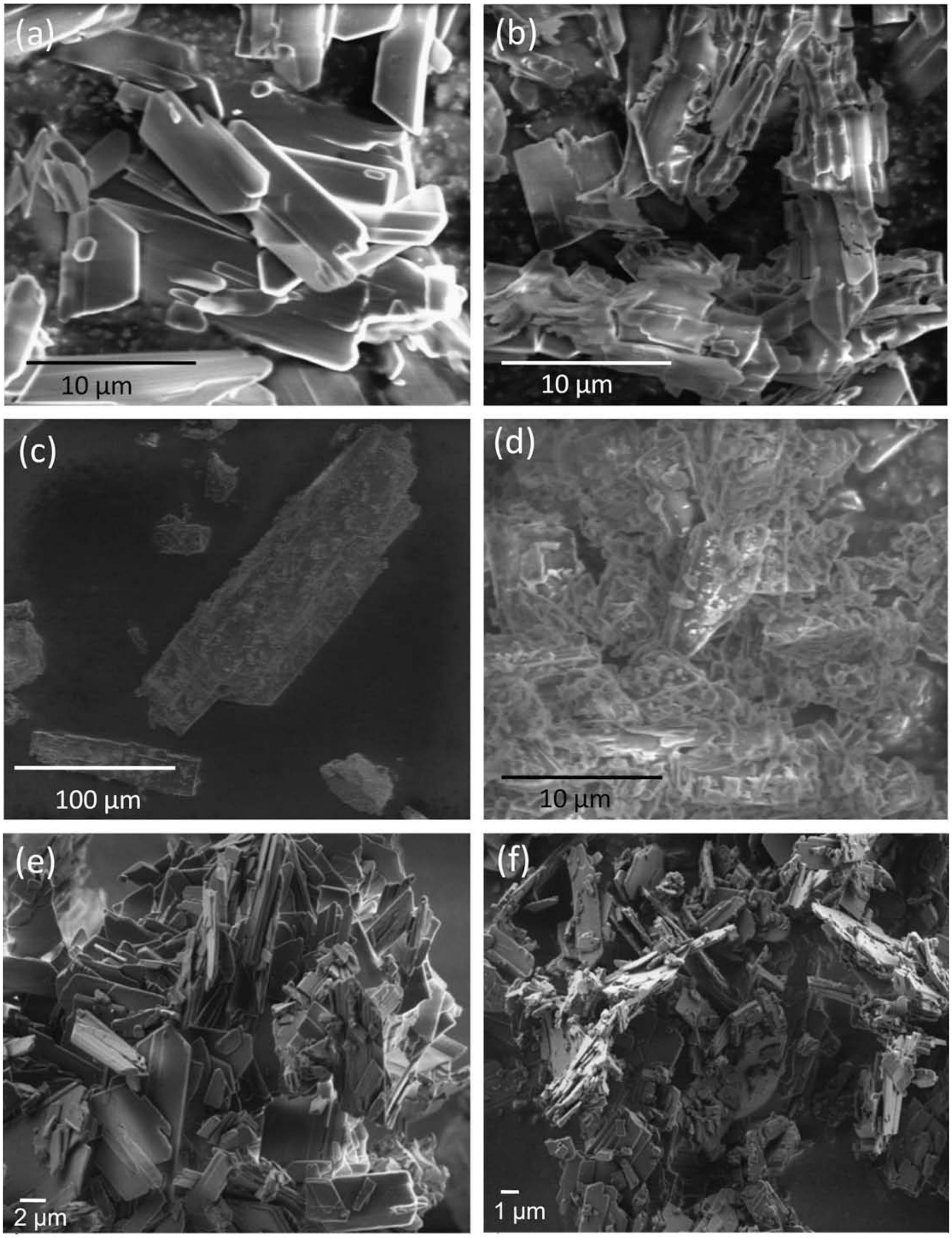


Fig. 5. SEM images of Cu-MOF (a), Cu-MOF-1 (b), Cu-MOF-lit (c), Cu-MOF-lit after reaction (d), Cu-MOF-as-prepared (e), and Cu-MOF-as-prepared after reaction (f).

allylic oxidation (entry 1) but the crystal-to-crystal restructuring during the complete dehydration under high vacuum is sufficient to provide a catalyst that is superior to the reference catalyst Cu-MOF-lit (entries 3–6). The small difference in the activities of Cu-MOF-1, CuMOF-2, Cu-MOF-3, and Cu-MOF-lit is probably related to differences in their particle size and thus the outer surface area of the particles. Note that a reliable determination of the BET surface areas is not possible due to restructuring (dehydration) of the framework during the necessary pretreatment at elevated temperature.

3.3. Nature of active sites

In the alcoholysis of epoxides, a rapid restructuring of Cu-MOF upon interaction with methanol was detected by spectroscopic methods [28]. This restructuring led to the formation of soluble $Cu_m bpy_n$-type oligomers that were highly active in the epoxide ring opening.

In contrast, for the oxidation of cyclohexene Cu-MOF was reusable with only a minor loss in the reaction rate (Table 1, entries 1 and 8). In addition, the conventional filtration test (continuation of the reaction after removal of the catalyst) was negative and ICP-OES analysis as well as EPR spectroscopy revealed no detectable Cu in the filtrate.

Fig. 6 shows the XRD patterns of Cu-MOF before and after reaction at 50 °C. The original crystalline structure of Cu-MOF was preserved during the reaction but a very weak new reflection at 16.5° (2θ) was detectable in the used sample. This reflection might be related to the presence of some organic residue on Cu-MOF.

In addition, ATR-IR investigation presented in Fig. 7 revealed no detectable restructuring of Cu-MOF in cyclohexene; all bands of Cu-MOF in cyclohexene can be attributed to either the catalyst or the reactant alone.

The experiments in Table 2 indicate the critical role of the structure of the catalyst in the oxidation of cyclohexene. Further evidence in this direction is that dehydration of Cu-MOF in high vacuum at 100 °C eliminated the catalytic activity (Table 2, entry 7). The dehydration opens the latent pores of Cu-MOF and increases to a large extent the accessible surface area and the amount of adsorbed CO_2, N_2, and Ar [46–48]. Unfortunately, this high surface area framework is inactive in our target reaction. The restructuring of Cu-MOF upon dehydration (Fig. 1b) is confirmed by ATR-IR spectroscopy (Fig. 8). The absence of structural water in the Cu-MOF-dehydrated (curve b) is evidenced by the disappearance of the OH stretching at 3489 cm^{-1} and 1700–2000 cm^{-1} originating from the hydrogen-bonding network of the solid. The two structures before dehydration (curve *a*) and after rehydration (curve *c*) are almost identical.

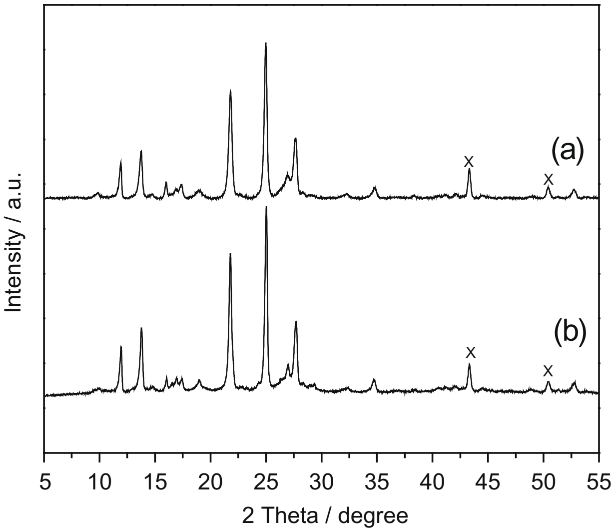


Fig. 6. XRD patterns of Cu-MOF before (a) and after (b) reaction at 50 °C; (x) marks diffraction peaks originating from the internal standard Cu.

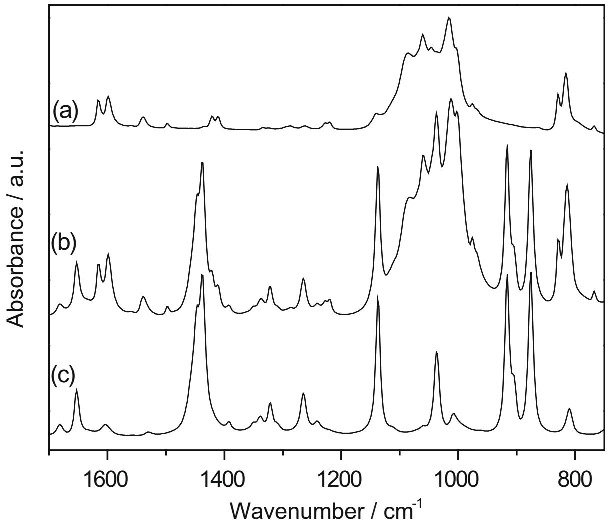


Fig. 7. ATR-IR spectra of samples at 50 °C under O_2 atmosphere: (a) Cu-MOF; (b) Cu-MOF in cyclohexene; and (c) cyclohexene.

All this information supports our interpretation that oxidation of cyclohexene with oxygen in the apolar reaction medium is a truly heterogeneous reaction and the surface Cu^{2+} sites of the latent-porous Cu-MOF are the active sites.

4. Discussion

The aim of the present work was to show the feasibility of the allylic oxidation of cyclohexene using molecular oxygen as the only oxidant and to clarify the real nature of the active sites. For this study it was advantageous to limit the conversion below 10% and avoid any solvent that could disturb the structural analysis. The solvent was replaced with the liquid substrate to mimic the usual conditions in a slurry reactor and under these conditions the conversion remained low even after long reaction times. The highest TON achieved at 45 °C in 15 h with the most active catalyst Cu-MOF-1 was 37 (Table 1). This value corresponds to a conversion of 8% and a formal turn-over frequency (TOF) of 2.5 h^{-1}, related to the total number of Cu sites in the catalyst. Although the conditions are not optimized to achieve high yield, the comparison below will show that Cu-MOF is a promising catalyst for the selective and environment-friendly allylic oxidation of cyclohexene.

Determination of the real TOF was not possible since the number of active Cu sites is unknown. The data presented in the previous chapter revealed that only the Cu sites at the outer surface of the latent porous material are accessible and take part in the oxidation process. Without pretreatment in vacuum at elevated temperature the BET method does not give reliable values and a pretreatment at or above 373 K induces a crystal-to-crystal restructuring including dehydration and opening of the micropores. Thus, after heat treatment the measured surface area includes the internal surface of the pores and this form of Cu-MOF is inactive in the oxidation reaction. It has been shown previously that the pretreatment temperature at 100–150 °C resulted in a variation of the BET surface area of Cu-MOF-lit in the range 1065–1426 m^2/g [47].

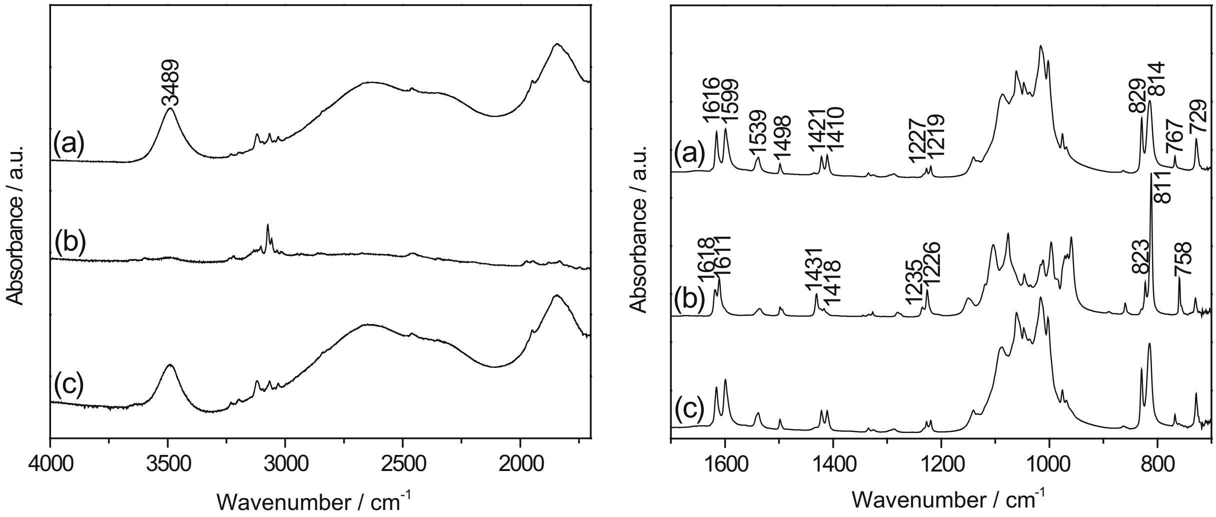


Fig. 8. ATR-IR spectra of Cu-MOF (a), Cu-MOF-dehydrated (b), and Cu-MOF-1 (c).

Another interesting feature of Cu-MOF is the considerable restructuring during reaction: stirring of the slurry induces a dramatic degradation of the original, regular-shaped particles to irregular shapes with particle sizes varying in a broad range. This phenomenon is best illustrated by the example of the structure of Cu-MOF-lit before and after the reaction (Fig. 5c and d). The very broad particle size distribution and the irregular shapes prevent the application of the commonly used statistical methods for the determination of the average particle size and thus calculation of the real TOF related to the surface active sites. Note, however, that in the literature the formal TOF related to the total amount of metal sites is commonly applied for characterization of the activity of MOFs.

To the best of our knowledge, Cu-MOF is the only metal–organic framework that has been found to be active in the oxidation of cyclohexene with molecular oxygen. Other Cu-, Cr-, or Co-containing MOFs (or coordination polymers) require for this transformation hydrogen peroxide in large excess [11,37] or TBHP [20,21,49]. The highest conversion (64.5%) and TOF (79 h^{-1}) were achieved with TBHP at 75 °C, but under the forcing conditions the catalyzed reaction was only twice as fast as the uncatalyzed oxidation [20]. MIL-101, a Cr-containing MOF was active in the allylic oxidation of α-pinene with molecular oxygen, but at 14% conversion the selectivities to the corresponding alcohol and ketone were only 14% and 7%, respectively. In addition, the solvent acetonitrile is not inert under oxidizing conditions and peroxycarboximidic acid may form, which is an active oxidizing species [50–52].

Considering the potential of MOFs in a broader perspective, there are several good examples in the recent literature on various catalytic oxidation reactions utilizing molecular oxygen as the only oxidant. These examples include the oxidative synthesis of α-hydroxy carbonyl compounds [18,19,53] and the facile oxidation of hydroquinone to p-benzoquinone [22] with Cu-based MOFs, the aerobic oxidation of alcohols with a Ru-containing MOF under ambient conditions [54], and the aerobic oxidation of tetralin with a Cu- and Co-containing MOF [16].

5. Conclusions

The Cu-MOF $[Cu(bpy)(H_2O)_2(BF_4)_2(bpy)]$ (bpy: 4,4′-bipyridine), with a 3D structure possessing no open pores, is an active and highly selective catalyst in the allylic oxidation of cyclohexene with molecular oxygen under mild, solvent-free conditions. The main product cyclohexene hydroperoxide is produced in 85–90% selectivity and epoxidation is a minor side reaction.

The active Cu^{2+} sites are located at the outer surface of the metal–organic framework. Dehydration of Cu-MOF, that is removal of the structural water, leads to the transformation of the original 3D interpenetrated-type MOF to a structure with direct coordination of all bpy ligands to Cu^{2+} ions, and to the complete loss of oxidation activity. Interestingly, also the homogeneous Cu-complex used as precursor for the catalyst synthesis was inactive. These results show the critical role of the structure of the active Cu^{2+} complex in the Cu-MOF. Although the reversible dehydration–rehydration of crystalline metal–organic frameworks is a known phenomenon [55–60], the present example is the first on the strikingly different catalytic behavior of the two crystalline forms.

The crystal-to-crystal restructuring of the framework accompanied by the dehydration–rehydration cycle results in a large enhancement of the oxidation activity of the as-prepared sample, which is probably due to the increased number of Cu^{2+} active site on the external surface of Cu-MOF and to the structural changes evidence by XRD.

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