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Copper-based metal-organic framework for the facile ring-opening of epoxides

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ABSTRACT

A simplified, facile route was applied for the synthesis of $Cu(bpy)(H_2O)_2(BF_4)_2(bpy)$ [Cu-MOF] from $Cu(BF_4)_2{\cdot}H_2O$ and 4,4′-bipyridine in aqueous ethanol. The Cu-MOF catalyst was characterized by XRD, elemental analysis, N_2 adsorption, SEM, TEM, and electron diffraction. The crystalline Cu-MOF is an efficient catalyst in the ring-opening reactions of epoxides with alcohols and aniline under ambient, solvent-free conditions. The catalytic activity of Cu-MOF was comparable to that of the homogeneous catalyst $Cu(BF_4)_2{\cdot}H_2O$ in the case of methanolysis, but the relative activity dropped significantly with increasing steric bulkiness of the alcohol, indicating the location of active sites in micropores. Although the catalyst was found to be truly heterogeneous and recyclable with no loss of activity, XRD revealed some restructuring due to interaction with methanol. This restructuring is attributed to the partial replacement of the structural water molecules by methanol, leading to significant changes in the H-bonding system of Cu-MOF.

1. Introduction

Metal-organic frameworks (MOFs), or coordination polymers, have generated great interest in the past decade as promising new materials for gas storage, separation, and heterogeneous (asymmetric) catalysis [1–6]. The mild synthetic methods allow the systematic tailoring of the structure and the chemical functional groups [7–9], and the resulting flexible framework can change its nanostructure to accommodate the reactants. An important characteristic of these solids is the "single-site" active species, where every active site is in an identical microenvironment due to the material's highly crystalline nature. These special features of MOFs allow simulating enzymes with the inherent advantages of heterogeneous catalysts. Recent catalytic applications include Knoevenagel condensation [10], cyclopropanation [11], epoxide isomerization [12], asymmetric hydrogenation [13,14], and various oxidation reactions [15–20]. Note, however, that in many MOFs the metal ions are saturated by coordinating organic ligands, and the real nature of active sites is poorly understood [18].

Blake et al. developed a novel Cu-based polymer, $Cu(bpy)(H_2O)_2(BF_4)_2(bpy)$ (Cu-MOF), with a hydrogen-bond regulated dynamic framework [21]. The Cu-MOF consists of two-dimensional sheets, each of which is composed of octahedral Cu(II) sites linked directly via coordinating 4,4′-bipyridine (bpy) units and also via bpy units and intermediate H-bonded water molecules (Fig. 1). The sheets are connected by the hydrogen bonding between an F atom of a BF_4^- 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 open structure is blocked. The involvement of the intermediate water molecules was attributed to the steric requirements of accommodating two BF_4^- anions of adjacent sheets [21]. Although the Cu-MOF has no open micropores and unsaturated coordination metal sites, it can adsorb CO_2 after partial thermal removal of water molecules [22,23] and gives high yields in the oxidation of trimethylsilyl enolates to α-hydroxy ketones using molecular oxygen as the oxidant [24,25].

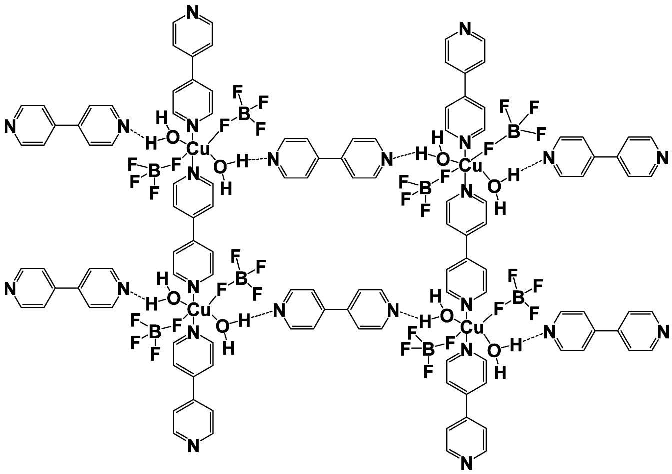

Fig. 1. Schematic representation of the *ab*-plane of the Cu-MOF crystal (according to Ref. [21]).

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The solvent diffusion method, commonly used for the synthesis of Cu-MOF [21–23,26], provides well-developed single crystals that are ideal for characterization; however, the procedure is time-consuming, and the product yield is low. We could well reproduce the fundamental framework structure of Cu-MOF by applying a simplified, convenient synthesis method. This Cu-MOF is a highly active, recyclable heterogeneous catalyst for the alcoholysis of epoxides.

2. Experimental

2.1. Chemicals

Hydrated Cu(II)-tetrafluoroborate (Cu: 21–22 mass%) and 4,4′-bipyridine (98%) were purchased from Aldrich. Methanol, *iso*-propanol, and *tert*-butanol were distilled from Mg before use. Benzyl alcohol (99%) was purchased from Aldrich and used without distillation. Aniline (99.5%), styrene oxide (98%), cyclohexene oxide (98%), cyclopentene oxide (98%), and 2-hexene oxide (97%) were purchased from Fluka; *trans*-stilbene oxide (99%) was purchased from Acros; and *cis*-stilbene oxide (98%) was purchased from Aldrich. The solvents (analytical grade) were used without further purification.

2.2. Synthesis of $Cu(bpy)(H_2O)_2(BF_4)_2(bpy)$ (Cu-MOF)

First, 4,4′-bipyridine (0.312 g; 2 mmol) in 2 mL of ethanol was slowly added to an 8-mL aqueous solution of $Cu(BF_4)_2{\cdot}H_2O$ (0.309 g; 1 mmol) at room temperature. The blue precipitate was formed gradually. The mixture was stirred for 4 h at room temperature, after which the solid was filtered off, washed with water and ethanol, dried in air at room temperature and then in vacuum at 100 °C (2 h), and stored under Ar.

2.3. Catalyst characterization

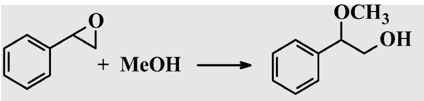
X-ray diffractograms were recorded on a Siemens D5000 powder diffraction system using Cu$K\alpha$ radiation (45 kV and 35 mA) and Cu as the reference. A Fa Leco CHN-900 instrument was used for C, H, and N elemental analysis. Nitrogen sorption isotherms were measured at 77 K on a Micromeritics ASAP 2000 system. The sample was outgassed at 373 K for 2 h under 10^{-3} Pa before the measurement.

Scanning electron microscopy (SEM) images were obtained on a Gemini 1530 (Zeiss) at low voltage ($U = 1$ keV). For transmission electron microscopy (TEM), the material was deposited onto a holey carbon foil supported on a copper grid. TEM and electron diffraction investigations were performed with a CM30ST microscope (FEI; LaB6 cathode, operated at 300 kV, point resolution $\sim$2 Å).

2.4. Catalytic reaction

The ring-opening reactions of epoxides were carried out in oven-dried glassware under air atmosphere. For the alcoholysis, 1.25 mmol of epoxide and the catalyst (Cu-MOF, 0.11 mmol Cu) were stirred in 5 mL of alcohol at room temperature for 2 h. The products were analyzed on an Agilent gas chromatograph equipped with a flame ionization detector and a HP-5 capillary column, with nonane used as the internal standard. The isolated yield was obtained by flash column chromatography on silica gel with petrol ether/ethyl acetate = 3/1 as the eluent (petrol ether/diethyl ether = 7:1 for stilbene oxide). The product was identified by GC-MS analysis. The *anti*/*syn* ratio was determined by ^{1}H NMR. The initial TOF was calculated from the conversion achieved in 2 h.

Table 1
Ring-opening of styrene oxide with methanol



Catalyst	Conv.[a] (%)	Sel.[a] (%)
Without catalyst	0	–
Cu-MOF	93	95.5
$Cu(BF_4)_2{\cdot}H_2O$	98	99
$Cu(BF_4)_2{\cdot}H_2O + 4$ equiv. Py	22	91
$Cu(BF_4)_2{\cdot}H_2O + 40$ equiv. Py	0	–

Note. Reaction conditions: catalyst (0.11 mmol Cu); CH_3OH (5 mL); styrene oxide (1.25 mmol); room temperature; 2 h; Py—pyridine.

[a] The conversion and selectivity values represent the average of three parallel reactions.

For the aminolysis reaction, 1.25 mmol of cyclohexene oxide and the catalyst Cu-MOF (0.11 mmol Cu) were stirred in 2 mL of aniline at room temperature. After 4 h, the catalyst was filtered off and the filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel using petrol ether/ethyl acetate (5/1) as eluent. The products were analyzed by GC and GC-MS.

Reaction conditions for the homogeneous copper salt were the same as described above, but using 0.11 mmol of copper salts instead of Cu-MOF.

3. Results and discussion

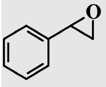
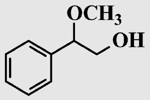
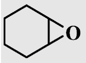
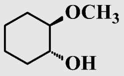
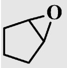
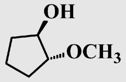
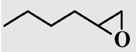
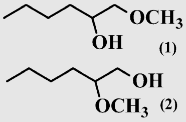
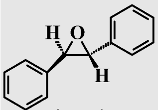
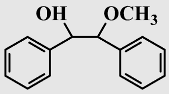
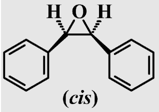
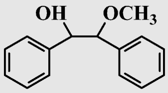
Here we first discuss the application of Cu-MOF as a Lewis acid catalyst for epoxide ring-opening, then summarize the characterization of the catalyst before and after the reaction.

3.1. Ring-opening reactions of epoxides

Cu-MOF is a highly active and selective heterogeneous catalyst in the alcoholysis of epoxides. The facile transformation of styrene oxide with methanol to 2-methoxy-2-phenylethanol is shown in Table 1. Conversion and selectivity >90% were achieved at room temperature in only 2 h, and no reaction occurred without the catalyst under the mild conditions. For comparison, the homogeneous catalyst $Cu(BF_4)_2{\cdot}H_2O$ was only slightly more active and selective than Cu-MOF. To mimic the effect of bipyridine ligands in Cu-MOF, we repeated the reaction with $Cu(BF_4)_2{\cdot}H_2O$ in the presence of four equivalent pyridine (Py). Clearly, the N-heteroaromatic compound deactivated the catalyst, and a further increase of the Py/Cu ratio up to 40 led to a complete loss of activity. This effect is due mainly to the coordination of Cu with pyridine, which hinders the access of styrene oxide to the Cu^{II} active sites. In the light of the poor activity of $Cu(BF_4)_2{\cdot}H_2O$ in the presence of pyridine, the excellent performance of Cu-MOF is even more impressive. Note that $Cu(BF_4)_2{\cdot}H_2O$ is an outstanding Lewis acid catalyst for various transformations, including ring-opening reactions of epoxides under very mild, solvent-free conditions [27–29]. In contrast, other Cu-containing MOFs tested in the alcoholysis of epoxides were either inactive [12] or required several days to complete the reaction at room temperature [30,31].

The reaction could be extended to aliphatic and cyclo-aliphatic epoxides (Table 2). The reaction rates, characterized by the turnover frequencies (TOF) calculated for the first 2 h, were lower than those for styrene oxide, but the selectivities to α-methoxy alcohols were always excellent, at least 95%. The structural effect on the rate of methanolysis was similar to that observed with the homogeneous catalyst $Cu(BF_4)_2{\cdot}H_2O$ (last column, values in brackets). Methanolysis of *trans*- and *cis*-stilbene oxide was slow and incomplete even after 3 and 6 days, respectively. The dramatic difference

Table 2
Ring-opening of various epoxides with methanol on Cu-MOF

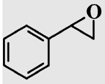
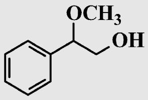
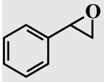
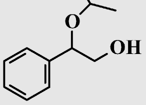
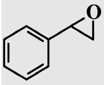
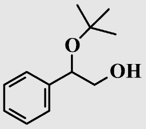
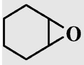
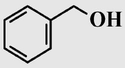
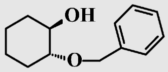
Epoxide	Product	Reaction time (h)	Conv. (%)	Isolated yield[a] (%)	Initial TOF[a] (h^{-1})
		3	99	94[b]	5.3 (5.6)
		9	99	95	4.4 (4.9)
		48	89	86	0.2 (0.3)
		48	66	65[c]	0.7 (1.0)
 **(*trans*)**		72	–	73[d] (100)	–
 **(*cis*)**		144	–	48[e] (100)	–

Note. Reaction conditions: catalyst (0.11 mmol Cu); alcohol (5 mL); epoxide (1.25 mmol); room temperature.

[a] Data in parenthesis are obtained with the homogeneous catalyst $Cu(BF_4)_2 \cdot H_2O$. Only alcoholysis products were found by GC/GC-MS; [b] GC yield.

[c] The ratio of the isomers (1)/(2) was 59/41; [d] *anti*:*syn* = 84:16; [e] *anti*:*syn* = 3:97.

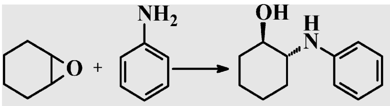
Table 3
Ring-opening of various epoxides with alcohols on Cu-MOF

Epoxide	Alcohol	Product	Reaction time (h)	Conv.[a] (%)	Initial TOF[a] (h^{-1})
	CH_3OH		3	99	5.3 (5.6)
	$(CH_3)_2CHOH$		2 24	5 (99.9) 15	0.3 (5.7)
	$(CH_3)_3COH$		2 24	4 (96) 19	0.2 (5.5)
			2 24	0.2 (99.9) 15	0.01 (5.7)

Note. Reaction conditions: catalyst (0.11 mmol Cu); alcohol (5 mL); epoxide (1.25 mmol); room temperature.

[a] Data in parenthesis are obtained with the homogeneous catalyst $Cu(BF_4)_2 \cdot H_2O$. Only alcoholysis products were found by GC/GC-MS.

Table 4
Ring-opening reaction of cyclohexene oxide with aniline



Catalyst	Isolated yield[a] (%)
Without catalyst	0
Cu-MOF	32
$Cu(BF_4)_2 \cdot H_2O$	62

Note. Reaction conditions: catalyst (0.11 mmol based on Cu); aniline (2 mL); epoxide (1.25 mmol); room temperature; 4 h.

[a] Isolated yield for Cu-MOF is the average value of three reactions; only the aminolysis product was found by GC/GC-MS.

between the reactivity of styrene oxide and stilbene oxides illustrates the effect of steric bulkiness on the reaction rate.

The differences between the heterogeneous and homogeneous copper catalysts were much greater when bulkier alcohols, such as *i*-PrOH, *t*-BuOH, and benzyl alcohol, were used (Table 3). In the corresponding reference reactions, $Cu(BF_4)_2 \cdot H_2O$ afforded 96–99.9% conversion within 2 h, independent of the size of the alcohol. The remarkable steric effects shown in Tables 2 and 3 provide indirect evidence for the heterogeneous nature of Cu-MOF, as we discuss later.

To illustrate that the activity of Cu-MOF was not limited to epoxide alcoholysis, we also give an example of the aminolysis: the reaction of cyclohexene oxide with aniline (Table 4). The isolated yield to the disubstituted amine was 32% in 4 h, only about 50% of that provided by the homogeneous catalyst $Cu(BF_4)_2 \cdot H_2O$. No detectable reaction occurred without the catalyst. The lower catalytic activity related to the homogeneous counterpart is likely due to diffusion limitations in the micropores of Cu-MOF. Also note that in the alcoholysis of cyclohexene oxide with benzyl alcohol, the steric bulkiness of the reactants was similar, but the reaction at the same temperature was much slower (Table 3, last row) than the aminolysis reaction.

3.2. Heterogeneity of Cu-MOF

The initial TOF in the reaction of cyclohexene oxide with methanol was about 90% of the initial TOF achieved with the homogeneous catalyst $Cu(BF_4)_2 \cdot H_2O$ (Table 2). Replacing methanol with the bulky benzyl alcohol decreased this ratio to only 0.2% (Table 3). Another remarkable steric effect can be seen in Table 2 by comparing the reactivity of styrene and stilbene oxides with methanol. This dramatic difference in the relative reactivities clearly demonstrates the location of the active sites in Cu-MOF in the micropores of the framework and indicates heterogeneous catalysis.

To confirm the heterogeneity of the reaction, the Cu-MOF was filtered off from the reaction mixture when the conversion of styrene oxide with methanol reached about 30% and 70%. The reaction was continued with the filtrate for 2 h, but no further conversion was observed (Fig. 2).

The reusability of Cu-MOF was investigated in the same reaction. As shown in Fig. 3, the good performance of Cu-MOF was maintained for at least up to four recyclings. A slight increase in conversion even occurred in the first recycling, which may be attributed to the formation of smaller particles due to the mechanical stress induced by the stirrer.

3.3. Structural stability of Cu-MOF during reaction

The literature suggests the limited chemical stability of MOFs under reaction conditions [32–34]. We used various physicochemical techniques to characterize the Cu-MOF before and after catalytic application. Elemental analysis of the unused Cu-MOF showed good agreement between the calculated and experimentally determined compositions. Table 5 also includes some data

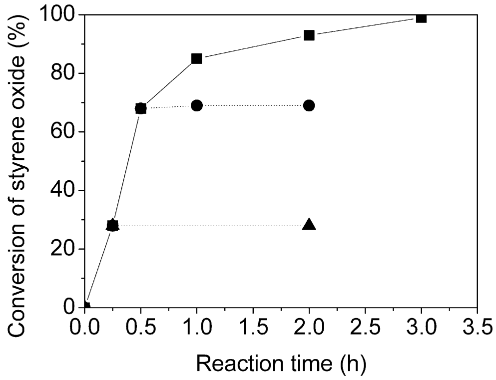


Fig. 2. Heterogeneity test: (■) Conversion of styrene oxide in the presence of Cu-MOF; (▲ and ●) No further conversion of styrene oxide after the catalyst was filtered off at 15 and 30 min.

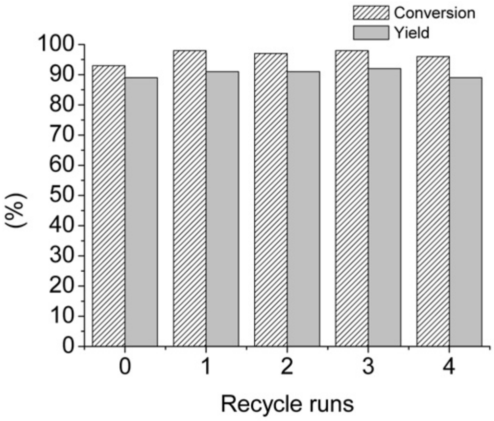


Fig. 3. Recycling tests on Cu-MOF in the ring-opening of styrene oxide with methanol (all reactions were run at least three times and the average conversion and yield are presented).

Table 5
Elemental analysis of Cu-MOF

	C (%)	H (%)	N (%)
Calculated	41.02	3.42	9.57
Found	41.18	3.45	9.48
From Ref. [21]	41.50	3.35	10.05
From Ref. [22]	41.24	3.50	9.59

reported previously for Cu-MOF prepared by the conventional method.

The adsorption behavior of nitrogen was similar to that reported for Cu-MOF [22,23]. Below a relative pressure (P/P_0) of about 0.10, the adsorbed amount of nitrogen was constant and almost zero (not shown). The sudden increase of the adsorbed amount at higher relative pressure (the so-called “gate pressure”) is attributed to a change in the H-bonding system leading to the formation of open micropores. A key element of the structural rearrangement during heat treatment before nitrogen adsorption is the partial removal of water molecules from the framework [22,23].

A typical scanning electron micrograph of Cu-MOF revealed a platelet-like crystal shape with particle size in the single-digit µm range (Fig. 4). TEM (Fig. 5a) confirmed that this crystal shape is characteristic of Cu-MOF; no other structures were found. Electron diffraction showed that Cu-MOF was crystalline, but that its structural stability was limited under strong electron beams (Fig. 5a). This observation is consistent with the flexible structure of Cu-MOF, as indicated by the restructuring during gas adsorption [22, 23]. The crystallinity decreased further after repeated use (Fig. 5b).

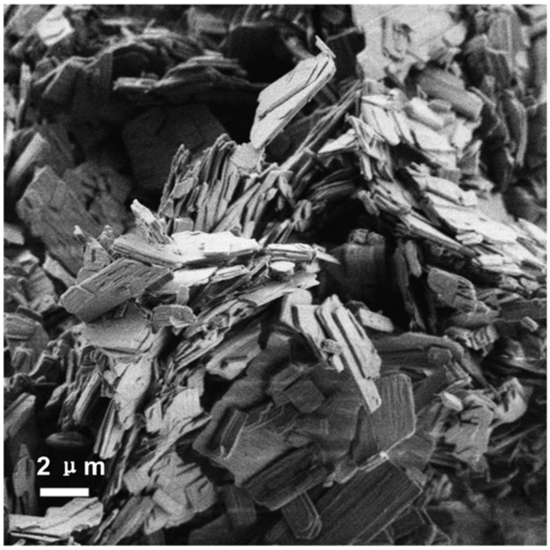


Fig. 4. SEM image of Cu-MOF before reaction.

The powder XRD pattern of the unused Cu-MOF catalyst revealed six characteristic strong diffraction peaks (at $2\Theta = 11.9$, 13.8, 21.8, 25.0, 27.0, 27.6) and several weak reflections in the range of 10–55 degrees (Fig. 6a). This XRD pattern is similar to that of Cu-MOF prepared by the conventional solvent diffusion method [23]. The different relative intensities of the peaks in the experimental diffractogram in Fig. 6a and the simulated XRD pattern reported by Blake et al. [21] (Fig. 6d) are attributed mainly to the preferred orientation of growth during Cu-MOF synthesis. Although some weak reflections in the simulated diffractogram are not seen in the experimentally observed diffractogram, the main peaks can be clearly identified.

Significant deviations can be seen between the diffractograms of the unused catalyst (Fig. 6a) and the catalyst after two recyclings (Fig. 6b). In the latter pattern, some reflections almost disappeared and a new peak appeared at about 11 degrees (2Θ) that was absent in the simulated pattern (Fig. 6d). For comparison, we studied the effect of methanol on the XRD pattern of Cu-MOF. The Cu-MOF catalyst was stirred in methanol for 2 h and then filtered off and dried in vacuum at 100 °C. After this treatment, the XRD pattern (Fig. 6c) was similar to that of the recycled catalyst (Fig. 6b) rather than that of the unused catalyst (Fig. 6a). The new diffraction peak at 11 degrees (2Θ) also was observed in the diffractogram of Cu-MOF after methanol treatment. We speculate that during soaking in methanol, a fraction of water molecules were replaced by methanol. This replacement should have a considerable influence on the H-bonding system of Cu-MOF, because some H atoms of the structural water molecules were formally replaced by a methyl group, resulting in some missing H-bridges between the two-dimensional sheets (Fig. 1).

4. Conclusion

A copper-containing metal-organic framework, Cu-MOF, was directly synthesized by a self-assembly reaction of $Cu(BF_4)_2 \cdot H_2O$ with 4,4′-bipyridine in aqueous ethanol. Structural characterization by XRD and elemental analysis confirmed that the crystal structure of this Cu-MOF was similar to that prepared by the conventional solvent diffusion method [21–23,26].

Cu-MOF is a highly active and selective Lewis acid catalyst in the ring-opening reaction of epoxides with methanol (Tables 1 and 2) at room temperature. The conventional filtration test and

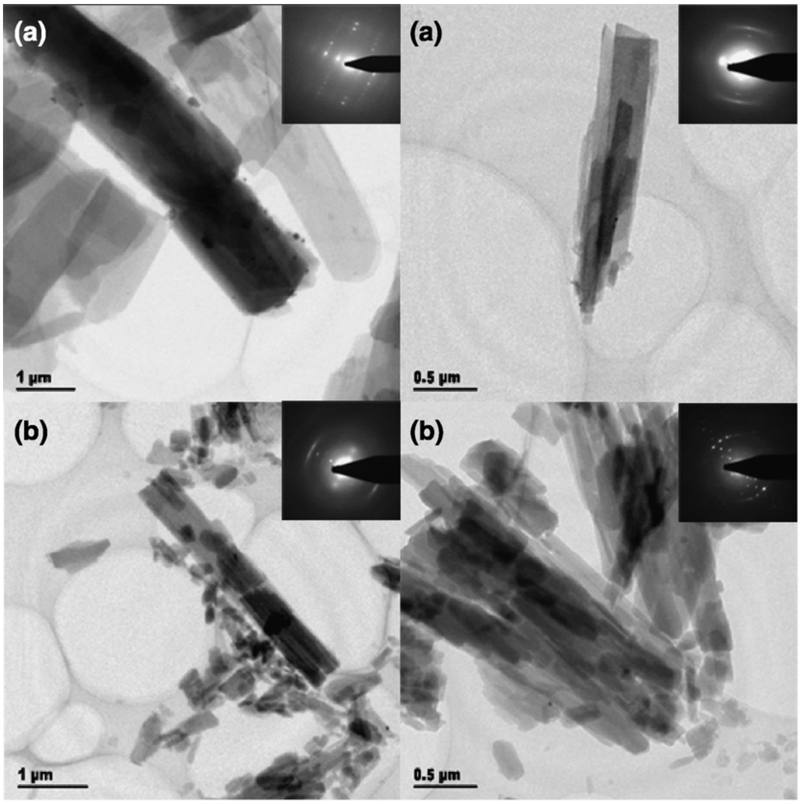


Fig. 5. Two examples on the restructuring of Cu-MOF followed by transmission electron microscopy and electron diffraction; (a) before reaction and (b) after the second recycling.

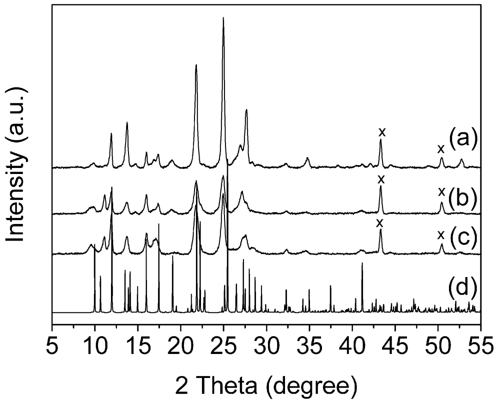


Fig. 6. XRD patterns of Cu-MOF (a) before reaction; (b) after the second recycling; (c) after methanol treatment; (d) the simulated XRD pattern taken from the literature [21]; (×) diffraction peaks originating from the internal standard Cu.

recycling experiments demonstrate that Cu-MOF is a truly heterogeneous, reusable catalyst. A preliminary study of the ring-opening of cyclohexene oxide with aniline (Table 4) indicates that Cu-MOF also may be useful in the aminolysis of epoxides. Based on the methanolysis reaction of epoxides, the present Cu-MOF was significantly more active than other copper-containing metal-organic frameworks [12,30,31]. The catalytic activity of Cu-MOF was comparable to that of the corresponding homogeneous catalyst $Cu(BF_4)_2 \cdot H_2O$, but only in the methanolysis reaction. When the styrene oxide was replaced by stilbene oxide, or when the small methanol reactant was replaced by more bulky alcohols, the activity dropped by about two orders of magnitude (Tables 2 and 3), clearly indicating the location of the Cu^{II} active sites in the narrow pores of the organic framework.

It is not yet possible to give an unambiguous explanation for the excellent performance of Cu-MOF in the methanolysis of epoxides. Cu-MOF prepared by the original method contains no open framework and no unsaturated Cu^{II} active sites [21]; however, it is active in the oxidation of trimethylsilyl enolates [24,25] and can adsorb CO_2 after thermal treatment at 75–150 °C [22,23]. The presence of water in the framework of Cu-MOF likely plays a key role in the high catalytic activity. The structural water, involved in H-bonding and the association of the two-dimensional sheets into a three-dimensional framework, provides additional flexibility. It may be partially replaced by methanol under reaction conditions, as indicated by our XRD findings (Fig. 6). Heat treatment before the reaction (in our case, at 100 °C in vacuum) is known to partially eliminate structural water and provide a microporous material [23]. Deactivation of the homogeneous catalyst $Cu(BF_4)_2 \cdot H_2O$ by pyridine also indicates that the Cu-MOF without the structural, H-bonding water may be less active. The assumption of this “dissociation–association” process of the framework structure during the catalytic reaction requires further investigation to rationalize the high activity of Cu-MOF under very mild conditions.

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References

[1] B. Kesanli, W.B. Lin, Coord. Chem. Rev. 246 (2003) 305.
[2] H.K. Ngo, W.B. Lin, Top. Catal. 34 (2005) 85.
[3] U. Mueller, M.M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, J. Mater. Chem. 16 (2006) 626.
[4] A.K. Cheetham, C.N.R. Rao, R.K. Feller, Chem. Commun. (2006) 4780.
[5] D. Maspoch, D. Ruiz-Molina, J. Veciana, Chem. Soc. Rev. 36 (2007) 770.

[6] U. Müller, M.M. Schubert, O.M. Yaghi, in: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Wiley–VCH, 2008, p. 247.
[7] C. Janiak, Dalton Trans. (2003) 2781.
[8] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334.
[9] S. Kitagawa, S. Noro, T. Nakamura, Chem. Commun. (2006) 701.
[10] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, J. Am. Chem. Soc. 129 (2007) 2607.
[11] M. Casarin, C. Corvaja, C. di Nicola, D. Falcomer, L. Franco, M. Monari, L. Pandolfo, C. Pettinari, F. Piccinelli, P. Tagliatesta, Inorg. Chem. 43 (2004) 5865.
[12] L. Alaerts, E. Seguin, H. Poelman, F. Thibault-Starzyk, P.A. Jacobs, D.E. De Vos, Chem. Eur. J. 12 (2006) 7353.
[13] A.G. Hu, H.L. Ngo, W.B. Lin, J. Am. Chem. Soc. 125 (2003) 11490.
[14] K.L. Ding, Z. Wang, L. Shi, Pure Appl. Chem. 79 (2007) 1531.
[15] W.A. Alves, S.A. de Almeida, R.H.D. Santos, A.M.D. Ferreira, Inorg. Chem. Commun. 6 (2003) 294.
[16] F. Xamena, A. Abad, A. Corma, H. Garcia, J. Catal. 250 (2007) 294.
[17] B. Xiao, H.W. Hou, Y.T. Fan, J. Organomet. Chem. 692 (2007) 2014.
[18] R.Q. Zou, H. Sakurai, S. Han, R.Q. Zhong, Q. Xu, J. Am. Chem. Soc. 129 (2007) 8402.
[19] A. Pramanik, S. Abbina, G. Das, Polyhedron 26 (2007) 5225.
[20] C. Di Nicola, Y.Y. Karabach, A.M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A.J.L. Pombeiro, Inorg. Chem. 46 (2007) 221.
[21] A.J. Blake, S.J. Hill, P. Hubberstey, W.S. Li, J. Chem. Soc. Dalton Trans. (1997) 913.
[22] D. Li, K. Kaneko, Chem. Phys. Lett. 335 (2001) 50.
[23] S. Onishi, T. Ohmori, T. Ohkubo, H. Noguchi, L. Di, Y. Hanzawa, H. Kanoh, K. Kaneko, Appl. Surf. Sci. 196 (2002) 81.
[24] T. Arai, H. Takasugi, T. Sato, H. Noguchi, H. Kanoh, K. Kaneko, A. Yanagisawa, Chem. Lett. 34 (2005) 1590.
[25] T. Arai, T. Sato, H. Kanoh, K. Kaneko, K. Oguma, A. Yanagisawa, Chem. Eur. J. 14 (2008) 882.
[26] A. Kondo, H. Noguchi, S. Ohnishi, H. Kajiro, A. Tohdoh, Y. Hattori, W.C. Xu, H. Tanaka, H. Kanoh, K. Kaneko, Nano Lett. 6 (2006) 2581.
[27] J. Barluenga, H. Vazquez-Villa, A. Ballesteros, J.M. Gonzalez, Org. Lett. 4 (2002) 2817.
[28] A. Kamal, R. Ramu, M.A. Azhar, G.B.R. Khanna, Tetrahedron Lett. 46 (2005) 2675.
[29] R.K. Khunger, Synlett (2006) 327.
[30] S.J. Hong, J.Y. Ryu, J.Y. Lee, C. Kim, S.J. Kim, Y. Kim, Dalton Trans. (2004) 2697.
[31] S.K. Yoo, J.Y. Ryu, J.Y. Lee, C. Kim, S.J. Kim, Y. Kim, Dalton Trans. (2003) 1454.
[32] K. Schlichte, T. Kratzke, S. Kaskel, Microporous Mesoporous Mater. 73 (2004) 81.
[33] T. Arai, T. Sato, H. Noguchi, H. Kanoh, K. Kaneko, A. Yanagisawa, Chem. Lett. 35 (2006) 1094.
[34] M. Sabo, A. Henschel, H. Froede, E. Klemm, S. Kaskel, J. Mater. Chem. 17 (2007) 3827.