DOI: 10.1002/cctc.201300529



Bimetallic–Organic Framework as a Zero-Leaching Catalyst in the Aerobic Oxidation of Cyclohexene

Ying-Ya Liu,^[a] Karen Leus,^[a] Thomas Bogaerts,^[a, b] Karen Hemelsoet,^[b] Els Bruneel,^[c] Veronique Van Speybroeck,^[b] and Pascal Van Der Voort^{*[a]}

A gallium 2,2'-bipyridine-5,5'-dicarboxylate metal-organic framework (MOF), denoted as COMOC-4, has been synthesized by solvothermal synthesis. This MOF exhibits the same topology as MOF-253. CuCl₂ was incorporated into COMOC-4 by a post-synthetic modification (PSM). The spectroscopic absorption properties of the MOF framework before and after PSM were compared with theoretical data obtained by employing molecular dynamics combined with time-dependent DFT calculations on both the as-synthesized and functionalized linker. The catalytic behavior of the resulting Cu²⁺@COMOC-4 materi-

Introduction

Catalyzed liquid-phase oxidation reactions are widely employed in industrial processes and are becoming increasingly important for the synthesis of fine chemicals.^[1] Among the different oxidation reactions, the epoxidation of olefins plays a prominent role as epoxides are highly reactive and versatile intermediates. Although homogeneous catalysts are still often utilized in industrial processes, there is an increasing interest in the employment of heterogeneous catalysts as they have a big advantage in terms of reuse and waste minimization. Metal-organic frameworks (MOFs) can be considered as potential candidates for use in catalysis.^[2] MOFs are 3D crystalline porous materials that consist of metal nodes connected by multifunctional organic linkers. Almost every transition metal ion and many different organic linkers can be used to obtain a MOF structure, which makes the plausible metal-ligand combinations endless.^[3] However, only a minor amount of MOFs are practi-

[a] Dr. Y.-Y. Liu, Dr. K. Leus, T. Bogaerts, Prof. Dr. P. Van Der Voort COMOC – Center for Ordered Materials, Organometallics and Catalysis Department of Inorganic and Physical Chemistry Ghent University Krijgslaan 281-53, 9000 Ghent (Belgium) Fax: (+ 32) 9-264-49-83 E-mail: pascal.vandervoort@ugent.be
[b] T. Bogaerts, Prof. Dr. K. Hemelsoet, Prof. Dr. V. Van Speybroeck Center for Molecular Modeling Ghent University Technologiepark 903, 9052 Zwijnaarde (Belgium)
[c] Dr. E. Bruneel SCRiPTs, Department of Inorganic and Physical Chemistry Ghent University

Krijgslaan 281-S3, 9000 Ghent (Belgium)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300529.

al was evaluated in the aerobic oxidation of cyclohexene with isobutyraldehyde as a co-oxidant. In addition, the catalytic performance of Cu²⁺@COMOC-4 was compared with that of the commercially available Cu-BTC (BTC = benzene-1,3,5-tricarboxy-late) MOF. Cu²⁺@COMOC-4 exhibits a good cyclohexene conversion and an excellent selectivity towards cyclohexene oxide in comparison to the Cu-based reference catalyst. Furthermore, no leaching of the active Cu sites was observed during at least four consecutive runs.

cally usable in catalysis as many of them show limited stability in typically employed catalytic reaction conditions.^[4] By pre-/ post-synthetic modification of the organic linker, complementary catalytic active sites can be introduced.^[5] Very recently we reported on the post-synthetic modification of V-NH₂-MIL-47 with TiO(acac)₂ (acac = acetylacetonate). The resulting NH₂-MIL-47[Ti] material exhibited a significantly higher stability and activity in the oxidation of cyclohexene compared to nonfunctionalized NH₂-MIL-47.^[5c]

In this study we looked for another MOF support that is more rigid in comparison to NH₂-MIL-47. Within this context, the bipyridine-based MOF-253, synthesized by Yaghi and coworkers,^[6] is an excellent candidate to serve as an MOF support. The beauty of this Al(OH)(bpydc) (bpydc²⁻=2,2'-bipyridine-5,5'-dicarboxylate) framework lies in the fact that the organic linkers offer free 2,2'-bipyridine sites, which are often employed as chelating ligands in coordination chemistry. More specifically, it can form metal complexes in which the metal is bound to the two N atoms to make it a bidentate-secured stable complex. Several attempts have been made to graft secondary metal sites on the bipyridine site by a post-synthetic modification approach. For example, Pd²⁺ and Cu²⁺ ions have been incorporated into the MOF-253 framework and were subsequently evaluated for their CO₂ uptake.^[6] Zou and co-workers have incorporated RuCl₃ into MOF-253, and the product was examined as a catalyst for the selective oxidation of primary and secondary alcohols.^[5b] In a very recent report of Li et al., Cu⁺ ions were incorporated into MOF-253 to catalyze the cross-coupling of phenols and alcohols with aryl halides.^[7]

In this contribution, we report on the catalytic performance of a member of the M(OH)(bpydc)series with M=Ga, denoted as COMOC-4 (COMOC=Center for Ordered Materials, Organo-

metallics and Catalysis, Ghent University), which we published recently.^[8] The MOF structure features an analogous structure to MOF-253 and is stable in air and water (50 $^\circ\text{C}$ for 24 h). CuCl₂, which shows a good binding affinity towards the bipyridine sites, was grafted on the COMOC-4 framework by postsynthetic modification (PSM). The spectroscopic properties of the MOF before and after PSM were elucidated by using ab initio simulations. In particular, molecular dynamics (MD) computations were performed on a model linker with and without Cu coordination to simulate the flexibility of the structures. Subsequently, time-dependent density functional theory (TD-DFT) was applied on snapshots extracted from the MD runs to compute an average UV/Vis spectrum. This methodology has been shown to be successful previously.^[9] The newly synthesized Cu²⁺@COMOC-4 was extensively evaluated as a bimetallic catalyst in the aerobic epoxidation of cyclohexene with an aldehyde as co-oxidant.^[10] Additionally, regenerability and stability tests were performed. Finally, the catalytic performance of Cu²⁺@COMOC-4 was compared with another Cu-based reference MOF, namely, Cu-BTC (BTC = benzene-1,3,5-tricarboxylate).

Results and Discussion

The powder XRD pattern of COMOC-4 (Figure S1, Supporting Information) reveals that this framework is isostructural with DUT-5^[11] (Al(OH)(bpdc), bpdc^{2–} = biphenyl-4,4'-dicarboxylate) as well as with MOF-253.^[6] The structure is indexed with orthorhombic unit cell parameters of a = 21.98(24), b = 7.302(8), and c = 17.470(24) Å. The COMOC-4 framework is constructed of infinite chains of octahedral GaO₄(OH)₂ units, in which each Ga³⁺ ion is bound to four bpydc^{2–} ligands and two μ_2 -trans hydroxide anions (Figure 1). This is a common coordination motif that has already been observed in a series of M³⁺ carboxylate frameworks (M = Al, Fe, V, Ga, and In).^[12] The GaO₄(OH)₂ chains are aligned parallel to the crystallographic *b* axis, and the hydroxide and carboxylate moieties alternate on either side of the chains, which are further linked to each other to form a 3D open framework (Figure S2). After the incorporation of CuCl₂



Figure 1. Representative structure of Cu^{2+} @COMOC-4. View along the 1D pore system. The structure model was generated based on the crystal structure of DUT-5 with 100% CuCl₂ occupancy.^[11]

into the COMOC-4 framework, the Bragg diffraction angles in COMOC-4 and Cu²⁺@COMOC-4 are essentially identical, which confirm that the COMOC-4 crystalline structure is preserved. After Cu incorporation, the intensity of the reflections decreased. The main difference is seen in the diffraction peak at 6.5° , which is related to the (101) planes that are parallel to the linkers (both directions are equivalent because of symmetry). The incorporation of CuCl₂ will induce slight changes in the shape and angle of the linkers. This results in several new Bragg reflections close to the original ones that are then merged together into one broader peak of lower intensity as observed in the XRD pattern.

The UV/Vis absorption spectra of the synthesized materials are presented in Figure 2 (top). The H₂bpydc ligand displays one absorption band centered at 299 nm, which arises from a π - π * transition in the aromatic rings. If the carboxylate linker is coordinated to Ga ions to form the COMOC-4 framework, the absorption spectrum exhibits a redshift of \approx 8 nm. In addition, the absorption band reveals a shoulder at 330 nm. For comparison, Cu(Me₂bpydc)Cl₂ was synthesized. As observed from the absorption spectra, the band that corresponds to the organic ligand is redshifted to 317 nm, whereas a shoulder peak appears at 334 nm and a broad band at 420 nm is observed, which indicates the metal-to-ligand coordination. Cu²⁺



Figure 2. UV/Vis absorption spectra of suspended Cu²⁺@COMOC-4 and COMOC-4 in MeOH solution compared to Cu(Me₂bpydc)Cl₂ and Me₂bpydc dissolved in MeOH (top); Solid-state UV/Vis spectra calculated from diffuse reflection spectra (bottom).

^{© 2013} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

@COMOC-4 exhibits two bands at 317 and 334 nm, which are in agreement with the absorption bands of Cu(Me₂bpydc)Cl₂. However, the absorption band that corresponds to the blue color is not visible because of the rather high background signal of the spectra recorded from the suspension. Diffuse reflection spectra (DRS) have also been measured from powder samples to get better resolution in the visible region. COMOC-4 has a broad, weak absorption band in the range of 430– 500 nm, whereas after incorporation of Cu²⁺ cations, a welldistinguished absorption band centered at 460 nm was observed (Figure 2 bottom).

The model used for the empty linker is shown in Figure 3. This is the most stable conformation.^[8] To allow $CuCl_2$ to coordinate to this ligand, both N atoms should be twisted to the same side as shown in Figure 3. Both models were optimized



Figure 3. Optimized structure of the protected linker ${\rm Me_2bpydc}$ and with coordinated ${\rm CuCl_2}.$

by using the B3LYP/6-311 + g(d) methodology to find their most stable conformations. UV/Vis spectra were calculated by using the computational method described below, which accounts for the flexibility of the structure. The main features from the experimental spectra are represented in the calculated dynamic spectra of Cu^{2+} coordinated to the bipyridine moiety compared with the as-synthesized linker. There is a slight shift to higher wavelengths, from 309 to 315 nm, but the shift is smaller in comparison to the experimental spectrum (299–317 nm; Figure 4a). The main absorption band for the empty linker (309 nm) is consistent with that shown before with static calculations.^[8] The shoulder at 338 nm (experimental spectrum)



Figure 4. a) Comparison between the calculated UV/Vis spectra of the protected Me₂bpydc linker and with Cu coordinated to the linker. The most important features of the experimental spectrum are indicated. b) Visualization of the orbitals involved in the metal-to-ligand electron transfer that corresponds to the visible excitation in the Cu-modified linker. The corresponding participation of the linker (in dark grey) and CuCl₂ (in light grey) fragments are also given.

tal: 334 nm) is also present and is a consequence of Cu²⁺ encapsulation. The broad peak around 450 nm is also visible in the ab initio spectrum, though this is shifted to a higher wavelength as compared to the measured result. To confirm that these changes are actually a result of metal coordination, one can take a closer look at the molecular orbitals involved in these excitations. The dominant orbitals involved in the excitation around 450 nm are displayed in Figure 4b and full details can be found in Figure S3. The orbitals and corresponding participation of the different fragments (Figure 4b) indicate that the coordinated metal contributes to the electronic transition. We can thus conclude that the observed changes in the UV/Vis spectrum are a result of the coordination of the CuCl₂ complex The two bands at 338 and 450 nm can be employed to reveal the successful incorporation of CuCl₂ in the MOF framework, which was clearly observed in the absorption spectra (334 nm) and UV/Vis DRS spectra (460 nm) of Cu²⁺@COMOC-4 UV/Vis (Figure 2 bottom).

COMOC-4 maintains a permanent microporosity after the removal of the guest molecules, as demonstrated by a type I N_2 sorption isotherm (Figure 5), and exhibits a Langmuir surface



Figure 5. N_2 adsorption (solid symbols) and desorption (open symbols) isotherms of COMOC-4 and $Cu^{2+}@COMOC-4$ at 77 K.

area of 920 m²g⁻¹. After the incorporation of CuCl₂, with a Cu/ Ga ratio of 0.4:1, 0.4Cu²⁺@COMOC-4 reveals a reduced Langmuir surface area of 630 m²g⁻¹. The thermal stability of COMOC-4 and 0.4Cu²⁺@COMOC-4 has been examined by thermogravimetric analysis (TGA; Figure 6). For COMOC-4, the first



Figure 6. TGA curves of COMOC-4 and $\mbox{Cu}^{2+}\mbox{@COMOC-4}$ measured in an air flow.

mass loss in the TGA profile corresponds to the elimination of water from the pores (\approx 6.5 wt%). COMOC-4 is thermally stable up to 300°C, above which a further weight loss of 62 wt% before 560 °C is indicative of the decomposition of the framework. The final residue (observed: 29.6 wt%, calculated 26.6 wt%) is Ga_2O_3 . The incorporation of Cu^{2+} decreases the thermal stability of the MOF framework; a similar behavior was observed in Ru@MOF-253.^[5b] The TGA profile of Cu²⁺ @COMOC-4 depicts the as-synthesized sample, the TGA curve shows a consistent weight loss of 11.5 wt% of solvent (water, methanol) release in the initial stage, and the delayed release (up to 200 °C) can be assigned to weakly bound methanol molecules, which are presumably held by weak forces (hydrogen bonds and van der Waals interactions) within the channels of the main framework as well as water molecules that are more firmly bound to the CuCl₂. A second major weight loss (62.5 wt%) occurs at 230 °C, which is attributed to the framework decomposition. The residue of 26.1 wt% (calculated: 27.6%) is Ga_2O_3 and CuO. Calculated values are based on the results of elemental analysis.

The aerobic epoxidation of cyclohexene in the presence of an aldehyde as co-oxidant was used in this study. Such liquidphase oxidation of cycloalkenes (or cycloalkanes) has been intensively studied by using MOF-based materials as catalysts. With variable active sites on MOF catalysts, and the use of different oxidants, this reaction can lead to different product distributions.^[13] Kholdeeva and co-workers^[13f] reported Cr- and Fe-MIL-101 materials as catalysts for the solvent-free selective oxidation of cyclohexane with O2 and/or tert-butylhydroperoxide (TBHP) as oxidant. The substrate conversion was in the range of 9-36% within 8 h, the major product formed can be cyclohexyl hydroperoxide or cyclohexanone. This strongly depends on the nature of the active metal. Kleist and co-worker $s^{[13a]}$ investigated the aerobic epoxidation of olefins ((*E*)-stilene and styrene) in a basic solvent (dimethylformamide, DMF), catalyzed by a Co-based MOF (STA-12(Co)). Different selectivities were obtained that depended on the substrates. The selectivity in styrene epoxidation was low because of substrate oligomerization. However, (E)-stilene was epoxidized with high selectivities between 80-90%. Garcia and co-workers^[13b] have reported the aerobic oxidation of cycloalkenes catalyzed by an Fe-based MOF in the presence of N-hydroxyphthalimide, and the cycloalkenes were mainly converted to allylic oxidation products. More recently, Xamena, Corma, and co-workers^[13e] have reported that MOFs with Cu^{2+} centers linked to four N atoms from azaheterocyclic compounds are active catalysts for the aerobic oxidation of activated alkanes. Furthermore, a tandem reaction was designed that used a Cu-MOF combined with silvlated Ti-MCM-41 as a solid catalyst, in which the Cu-MOF first catalyzed cumene oxidation to form cumene hydroperoxide as the major product, and the intermediate hydroperoxide together with silylated Ti-MCM-41 further catalyzed 1-octene to obtain 1-octene oxide. However, at high temperatures (90°C) the presence of Cu-MOF will catalyze the 1-octene at the allylic position. Therefore, to increase the selectivity to the epoxide product, 1-octene and the Cu-MOF were kept in separate reactors. In the present work, we further explore the catalytic activity of Cu-MOFs in the epoxidation of alkenes by the Mukaiyama system.^[14]

All our catalytic tests on the Cu-based MOFs were performed under identical reaction conditions to allow a fair comparison (see Table 1). Cu-BTC, a copper trimesate $Cu_3(BTC)_2(H_2O)_3$, known as HKUST-1, and commercially available as Basolite C300, was applied as a reference catalyst. This material forms face-centered cubic crystals that contain an intersecting 3D system of large square-shaped pores (9×9 Å).

The TON and TOF values of the two Cu-based MOFs are depicted as a function of the reaction time in Figure 7. Cu^{2+} @COMOC-4 and Cu-BTC show a good catalytic performance as evidenced by the linear increase in the TON. Nevertheless, Cu^{2+} @COMOC-4 has a much higher TON value than Cu-BTC. After 7 h of catalysis, the TON value of Cu-BTC is 75, whereas Cu^{2+} @COMOC-4 exhibits a TON value of almost 138. Moreover, it can be seen that both catalysts reach a plateau in their TOF

Table 1. Results of the epoxidation of cyclohexene catalyzed by Cubased compounds.								
Catalyst		Conv. [%]	Sel. [%]	TOF [h ⁻¹]	Leaching [%]	Bypi sele 3 ^[c]	roduc ctivity 4 ^[c]	t [%] 5 ^[c]
Cu ²⁺ @COMOC-4 ^[a]	1 st run	49.0	89.0	21.5	0	4.3	2.6	3.9
	2 nd run	46.2	87.0	19.7	0	5.3	3.1	4.5
	3 rd run	41.5	87.8	18.9	0	5.6	3.1	3.4
	4 th run	41.6	89.2	18.0	0	5.1	2.7	2.9
Cu-BTC		41.7	77.5	11.1	13.2	6.9	8.5	7.0
COMOC-4 ^[b]		11.4	52.5	2.7	0	-	-	-

[a] Reaction conditions: $Cu^{2+}@COMOC-4$ (0.19 g in the first run, 0.2 mmol Cu sites), chloroform (40 mL), substrate (7 mL), isobutyraldehyde (11.4 mL), O_2 (7.7 mLmin⁻¹), T=313 K, t=7 h. [b] Based on Cu²⁺ @COMOC-4, an equal amount of Ga sites (0.65 mmol) was used, and the TOF was calculated based on the number of moles of Cu sites. [c] Refer to Scheme 1 for product distributions.



Figure 7. Catalytic activity expressed as TON (top) and TOF (bottom) for $Cu^{2+}@COMOC-4$ (1) and Cu-BTC (2). Reaction conditions: 0.2 mmol Cu sites, 50 mmol cyclohexene, 100 mmol isobutyraldehyde, 40 mL chloroform, T=40 °C, O₂ flow: 7.7 mLmin⁻¹.

value after nearly 1 h of catalysis (Figure 7 bottom). The TOF value of Cu-BTC is approximately 12 h⁻¹, whereas for Cu²⁺ @COMOC-4, a significantly higher TOF value of nearly 22 h⁻¹ is noted, which demonstrates that Cu²⁺@COMOC-4 converts cy-clohexene much faster in comparison to the reference catalyst.

As presented in Table 1, both Cu-based catalysts gave cyclohexene oxide as the predominant product (Scheme 1, pathway a). $Cu^{2+}@COMOC-4$ shows a remarkable catalytic activity to afford 49% of cyclohexene conversion after 7 h of catalysis with a selectivity of 89% towards the epoxide in the first run (Figure S4). No leaching of Cu and Ga sites was detected during the first run, which indicates that the catalysis occurs truly heterogeneously. In contrast to $Cu^{2+}@COMOC-4$, for Cu-BTC, although the XRD pattern indicates no obvious changes in crystallinity after catalysis (Figure S5), a rather high Cu leach-



Scheme 1. Oxidation of cyclohexene (1) towards the main reaction products: a) epoxidation to cyclohexene oxide (2), b) allylic oxidation to 2-cyclohexene-1-one (3) and 2-cyclohexen-1-ol (4), c) consecutive ring opening to cyclohexane-1,2-diol (5).

ing of 13.2% was detected after catalysis, which clearly demonstrates that the catalytic activity of Cu-BTC is mainly a result of homogeneous catalysis.

Additionally, the recyclability and stability of Cu²⁺@COMOC-4 was evaluated. In total, four successive runs were performed on Cu²⁺@COMOC-4. The results of the consecutive runs are presented in Table 1 and Figure S6. Although there is a slight reduction in the cyclohexene conversion during the additional runs, the TOF value remains fairly constant. This observation demonstrates the good recyclability of Cu²⁺@COMOC-4. The slight decrease in the observed cyclohexene conversion is probably because of a small loss of catalyst after each run. Moreover, the selectivity towards the epoxide stays fairly constant in the additional runs. Besides cyclohexane-1,2 diol, which is the result of epoxide opening owing to the presence of trace amounts of water adsorbed on the hydrophilic MOFs, 2-cyclohexen-1-ol and 2-cyclohexen-1-one are the observed byproducts during each catalytic test. The formation of these byproducts is a result of the allylic oxidation of cyclohexene.^[10c, 15] No leaching of Cu and Ga species was observed during these successive runs, which demonstrates the stability and regenerability of the catalyst. The powder XRD patterns of the Cu²⁺@COMOC-4 catalyst before and after each consecutive run are presented in Figure 8. It can be seen that the structural integrity of the framework is well preserved during these four following runs.

The Cu-BTC catalyst, which also contains unsaturated Cu sites, exhibits a similar product distribution and cyclohexene conversion (41.7% for Cu-BTC and 49% for Cu²⁺@COMOC-4), however, a difference in selectivity was detected between the catalysts. In contrast to Cu²⁺@COMOC-4, which has an average selectivity of 89% towards the epoxide, Cu-BTC exhibits a lower selectivity of 77.5% towards cyclohexene oxide, which results from the formation of a larger amount of byproducts (2-cyclohexene-1-one (3), 2-cyclohexen-1-ol (4), and cyclohexane-1,2-diol (5)). This could be because of the different structure of the Cu-MOF in comparison to Cu²⁺@COMOC-4. The Cu paddlewheel units in Cu-BTC contain unsaturated Cu sites that favor the binding of water. The presence of this adsorbed water can play a prominent role in the ring opening of the epoxide.^[16] Moreover, the paddlewheel structure has been shown to have a catalytic influence on epoxide ring-opening reactions.[16b]

^{© 2013} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 8. XRD patterns of Cu²⁺@COMOC-4 before and after each catalytic run. (The peak at 32.9° is because of the background of the silicon sample holder)

The reaction mechanism for the transition-metal-catalyzed aerobic oxidation of alkenes in the presence of an aldehyde as a co-reagent is widely known in the literature as the Mukaiya-ma–Yamada epoxidation reaction (Scheme 2).^[14] In this study,



Scheme 2. Main mechanism to catalyze cyclohexene epoxidation in the presence of O_2 and isobutyraldehyde.

the autoxidation of the aldehyde plays a critical role in the catalytic process. Without the aldehyde, the Cu²⁺-catalyzed alkene reaction is more in favor of the allylic reaction pathway.^[13e, 17] The co-reactant isobutyraldehyde is transformed in situ into an acylperoxy radical, which is the predominant oxidizing species and facilitates the oxygen transfer to the olefin. Cyclohexene is a good substrate to investigate whether the oxidizing species prefers allylic oxidation or epoxidation.^[15] The acylperoxy radicals preferentially react with the double bond of the alkenes to yield the epoxide (Scheme 3). The latter pathway is the major reaction pathway observed during our catalytic tests, which indicates that the Cu²⁺ active sites mainly sta-



Scheme 3. The alkylperoxy radicals generated in the main catalytic cycle lead to the formation of byproducts (pathway b) in addition to cyclohexene oxide (pathway a). Adapted from Ref. [15a].

bilize the acylperoxy radical. Afterwards, the unstable carboxyl radical decomposes to form an alkyl radical, which can in turn be oxidized to an alkylperoxy radical. This species is less selective towards the formation of epoxides and leads to the formation of byproducts through the allylic oxidation pathway (Scheme 3, pathway b).

Conclusions

A Ga-based metal–organic framework (MOF), denoted as COMOC-4, has been successfully synthesized and characterized. In a second step $CuCl_2$ was incorporated into COMOC-4 by a post-synthetic modification approach. The successful incorporation was verified with the aid of ab initio techniques. The catalytic performance of the resulting $Cu^{2+}@COMOC-4$ material was investigated for the aerobic oxidation of cyclohexene in the presence of the co-oxidant isobutyraldehyde. In comparison to Cu-BTC (BTC=benzene-1,3,5-tricarboxylate), $Cu^{2+}@COMOC-4$ shows the best catalytic performance in terms of selectivity towards cyclohexene oxide. Furthermore, no leaching of either Ga or Cu species was detected over four successive runs, which indicates the good stability and reusability of the catalyst.

Experimental Section

General

The 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpydc) ligand was prepared according to a procedure published elsewhere.^[18] Commercially available spectroscopic grade methanol was applied for the spectroscopic studies. All the other starting materials (analytical grade) were bought and used without further purification. Cu-BTC (BasoliteTM C300, Sigma–Aldrich) as well as the as-synthesized porous compounds were activated at 120 °C under vacuum for 3 h prior to use.

Synthesis

Synthesis of the Cu complex: [Cu(Me₂bpydc)]Cl₂(H₂O)_{1.5}

The dimethyl-(2,2'-bipyridine)-5,5'-dicarboxylate (Me₂bpydc) ligand was synthesized according to the procedure described by Gunyar et al.^[19] In a second step, Me₂bpydc (0.03 g) and CuCl₂·2H₂O (0.019 g) were mixed in a Pyrex tube with methanol (5 mL). The Pyrex tube was subsequently heated to 120 °C and kept at this temperature overnight. The blue powder was collected by filtra-

CHEMCATCHEM FULL PAPERS

tion, washed with acetone, and dried under vacuum. Elemental analysis calcd (%) for $CuCl_2$ (CH_3)₂($C_{12}H_6O_4N_2$)·1.5 H_2O (433.73): C 41.49, H 2.70, N 6.24; found: C 41.24, H 2.90, N 6.77.

Synthesis of COMOC-4 (Ga(OH)(bpydc))

The synthesis of COMOC-4 was optimized at the gram scale based on our earlier reported synthesis procedure.^[8] Ga(NO₃)₃·H₂O (1.2 g, 4.4 mmol) and H_2 bpydc (1.2 g, 5 mmol) were added to DMF (120 mL) in a 250 mL Schlenk flask equipped with a magnetic stirrer. In the first instance, the mixture was heated to 110 °C and kept at this temperature for 0.5 h. Afterwards the mixture was further heated to 150 °C and held at this temperature for 48 h with gentle stirring. An orange powder was collected over a membrane filter and washed thoroughly with DMF, methanol, and acetone. For the removal of unreacted linker from the pores, the solid product was suspended in DMF (0.5 g per 50 mL DMF), heated at 80 $^\circ\text{C}$ for 2 h, collected by filtration, washed with DMF and acetone, and dried under vacuum. To ensure the complete exclusion of the organic species encapsulated within the pores of the open framework, a Soxhlet extraction in methanol was performed over 48 h at 120 °C. Afterwards the COMOC-4 material was dried under vacuum overnight at RT. As a result of the presence of the -OH moiety on the Ga building unit, the 1D channels are highly hydrophilic. For this reason, the activated sample was stored under an inert atmosphere. The yield was 33% based on the Ga source. IR (KBr pellet): $\tilde{v} =$ 3379 (br), 1619 (s), 1595 (s), 1421 (s), 1394 (s), 1158 (w), 1050 (w), 847 (w), 775(m), 705 (w), 600 (w), 479 cm⁻¹ (w); elemental analysis calcd (%) for Ga(OH)($C_{12}H_6N_2O_4$)·2.7 H_2O (377.56): C 38.36, H 3.27, N 7.46; found: C 38.26, H 3.12, N 7.17.

Grafting the CuCl₂ complex onto the COMOC-4 framework

Cu²⁺@COMOC-4 was prepared by stirring Ga(OH)(bpydc) (0.5 g) and CuCl₂·2 H₂O (0.1 g) in absolute methanol (30 mL) at 50 °C for 6 h. The green MOF powder was collected by filtration and was stirred in pure methanol (20 mL) for 6 h followed by filtration. This procedure was repeated twice to guarantee the complete removal of physisorbed CuCl₂ salts.

Characterization

Powder XRD and TGA

Powder XRD patterns were recorded by using a Thermo Scientific ARL X'Tra diffractometer, operated at 40 kV, 40 mA using CuK_{\alpha} radiation ($\lambda = 1.5406$ Å). TGA data were obtained by using a Netzsch STA 449 F3 Jupiter-Simultaneous TG-DSC analyzer with a heating rate of 10°Cmin⁻¹ in air. N₂ sorption measurements were performed by using a Belsorp II, Bell Japan, Inc. All the samples were activated under vacuum at 120°C for 3 h prior to analysis.

Spectroscopic characterization

FTIR spectra were recorded in the region of 400–4000 cm⁻¹ by using a Bruker EQUINOX 55 FTIR spectrometer. UV/Vis absorption spectra were collected by using a Perkin–Elmer Lambda 950 UV/Vis spectrometer in the range of 260–900 nm. The spectra were recorded by using fine suspensions of powder samples (COMOC-4 and Cu²⁺@COMOC-4) in methanol. In a typical measurement, 4 mg of powder sample was suspended in 3 mL of methanol in an ultrasonic bath for 5 min. The suspension was transferred to a 10 mm

path length quartz cuvette to record the spectrum. The UV/Vis DRS experiments were performed by using a Hitachi U-3000 UV/VIS Spectrophotometer with a diffuse reflectance accessory (integrated sphere) for spectrophotometric measurements in the range of 350–800 nm. The spectra were converted by using the Kubelka-Munk function. X-ray fluorescence spectrometry (XRF) measurements were performed by using a Rigaku NexCG, Energy Dispersive X-ray Fluorescence (EDXRF) instrument.

Computational methodology

MD simulations were performed on the linker with and without Cu coordination in a vacuum box of 20×20×20 Å by using the CP2K package.^[20] All DFT calculations were performed by using the Gaussian plane waves (GPW) method,^[21] with a DZVP basis set, GTH pseudopotentials,^[22] and the BLYP functional. MD runs were conducted by using the canonical (NVT) ensemble at 300 K with a time step of 1 fs. A chain of five Nosé-Hoover thermostats was used to control the temperature. The system was first allowed to equilibrate after which a simulation of 20 ps was used for analysis. The dynamic UV/Vis spectra were obtained by taking 100 snapshots from the simulation on which vertical TD-DFT calculations were performed. This methodology has previously proven valuable for the simulation of absorption spectra.^[9,23] An average optical spectrum was then obtained. The influence of the methanol solvent was included with a polarizable continuum model (PCM). All TD-DFT calculations were performed by using the Gaussian $09^{\scriptscriptstyle [24]}$ program using the B3LYP^[25] functional and a 6-311⁺G(g) Pople basis set. We previously demonstrated that the B3LYP functional is very efficient for these types of systems.^[8] The effect of relativistic contributions was found to be small, and full details are given in the Supporting Information.

Catalysis

The oxidation of cyclohexene was performed in a 100 mL glass reactor equipped with a reflux condenser with recirculating cooling at -4°C. In a typical catalytic test, the reactor was loaded with Cu²⁺@COMOC-4 (0.19 g, 0.2 mmol Cu active sites), cyclohexene (7 mL, 5 mmol), isobutyraldehyde (11.4 mL), chloroform (40 mL), and 1,2,4-trichlorobenzene (9 mL) employed as an internal standard. The molar ratio of cyclohexene/co-oxidant (isobutyraldehyde) was 1:2. The O_2 flow rate was set to 7.7 mLmin⁻¹ by using a mass flow controller. All the catalytic tests were performed at 40 °C. Blank reactions at this temperature showed no formation of oxidation products. During the catalytic tests, aliquots were gradually taken out of the mixture, diluted with ethyl acetate (500 µL), and subsequently analyzed by GC with flame ionization detection (FID). The reaction products were identified by using a TRACE GC×GC (Thermo, Interscience) coupled to a TEMPUS TOF-MS detector (Thermo, Interscience). The first column consists of a dimethyl polysiloxane packing and has a length of 50 m with an internal diameter of 0.25 mm, and the second column has a length of 2 m with an internal diameter of 0.15 mm. The packing of the latter is a 50% phenyl polysilphenylene siloxane. He was used as the carrier gas with a constant flow (1.8 mLmin^{-1}) .

All the fresh catalysts were activated under vacuum at 120 °C for 3 h prior to catalysis. After each catalytic run, the catalyst was recovered by filtration, washed with acetone, and dried at RT overnight under vacuum to reuse it in another run. To investigate the recyclability of the Cu²⁺@COMOC-4 catalyst, four consecutive runs were performed. Moreover, to examine the heterogeneity of the

catalyst, the filtrate, after the removal of the catalyst, was analyzed by XRF to quantify the possibly leached Cu and Ga species.

Acknowledgements

The authors acknowledge the financial support from the Ghent University BOF Grant (Nr. 01P02911T), GOA Grant (01G00710) and the Long Term Structural Methusalem grant nr. 01M00409 Funding by the Flemish Government. Furthermore, this research is co-funded by BELSPO in the frame of IAP 7/05 and the European Research Council (FP7(2007-2013) ERC Grant (Nr. 240483). Computational resources and services were provided by Ghent University.

Keywords: ab initio calculations · copper · epoxidation · heterogeneous catalysis · metal–organic framework

- [1] a) A. Corma, J. Catal. 2003, 216, 298–312; b) J. H. Clark, D. J. Macquarrie, Org. Process Res. Dev. 1997, 1, 149–162.
- [2] a) J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* 2009, *38*, 1213–1214; b) K. K. Tanabe, S. M. Cohen, *Chem. Soc. Rev.* 2011, *40*, 498–519; c) J. L. C. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.* 2004, *73*, 3–14.
- [3] a) M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* 2001, *34*, 319–330; b) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* 1998, *31*, 474–484.
- [4] a) A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Catal. Sci. Technol.* 2011, *1*, 856–867; b) V. Van Speybroeck, K. Leus, I. Muylaert, M. Vandichel, G. B. Marin, M. Waroquier, P. Van der Voort, *Chem. Commun.* 2010, *46*, 5085–5087; c) A. Corma, H. Garcia, F. X. Llabres i Xamena, *Chem. Rev.* 2010, *110*, 4606–4655.
- [5] a) L. Ma, J. M. Falkowski, C. Abney, W. Lin, *Nat. Chem.* 2010, *2*, 838–846;
 b) F. Carson, S. Agrawal, M. Gustafsson, A. Bartoszewicz, F. Moraga, X. Zou, B. Martin-Matute, *Chem. Eur. J.* 2012, *18*, 15337–15344; c) K. Leus, G. Vanhaelewyn, T. Bogaerts, Y.-Y. Liu, D. Esquivel, F. Callens, G. B. Marin, V. Van Speybroeck, H. Vrielinck, P. Van Der Voort, *Catal. Today*, 2013, *208*, 97–105.
- [6] E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long, O. M. Yaghi, J. Am. Chem. Soc. 2010, 132, 14382–14384.
- [7] M. Wang, B. Yuan, T. Ma, H. Jiang, Y. Li, RSC Adv. 2012, 2, 5528-5530.
- [8] Y.-Y. Liu, R. Decadt, T. Bogaerts, K. Hemelsoet, A. M. Kaczmarek, D. Poelman, M. Waroquier, V. Van Speybroeck, R. Van Deun, P. Van Der Voort, J. Phys. Chem. C 2013, 117, 11302–11310.
- [9] a) T. De Meyer, K. Hemelsoet, L. Van der Schueren, E. Pauwels, K. De Clerck, V. Van Speybroeck, *Chem. Eur. J.* **2012**, *18*, 8120–8129; b) V. Barone, J. Bloino, S. Monti, A. Pedone, G. Prampolini, *Phys. Chem. Chem. Phys.* **2010**, *12*, 10550–10561; c) K. Hemelsoet, Q. Qian, T. De Meyer, K. De Wispelaere, B. De Sterck, B. M. Weckhuysen, M. Waroquier, V. Van Speybroeck, Chem. Eur. J. 2013, doi: 20.1002/chem.201301965.
- [10] a) B. Monteiro, S. Gago, S. S. Balula, A. A. Valente, I. S. Gonçalves, M. Pillinger, J. Mol. Catal. A 2009, 312, 23–30; b) M. Nandi, P. Roy, H. Uyama,

A. Bhaumik, *Dalton Trans.* **2011**, *40*, 12510–12518; c) N. Komiya, T. Naota, Y. Oda, S.-I. Murahashi, *J. Mol. Catal. A* **1997**, *117*, 21–37.

- [11] I. Senkovska, F. Hoffmann, M. Froba, J. Getzschmann, W. Bohlmann, S. Kaskel, *Microporous Mesoporous Mater.* 2009, 122, 93–98.
- [12] a) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Ferey, *Chem. Eur. J.* **2004**, *10*, 1373–1382; b) A. J. Jacobson, M. Vougo-Zanda, J. Huang, E. Anokhina, X. Q. Wang, *Inorg. Chem.* **2008**, *47*, 11535–11542.
- [13] a) M. J. Beier, W. Kleist, M. T. Wharmby, R. Kissner, B. Kimmerle, P. A. Wright, J.-D. Grunwaldt, A. Baiker, *Chem. Eur. J.* 2012, *18*, 887–898; b) A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *J. Catal.* 2012, *289*, 259–265; c) N. V. Maksimchuk, K. A. Kovalenko, V. P. Fedin, O. A. Kholdeeva, *Chem. Commun.* 2012, *48*, 6812–6814; d) A. M. Balu, C. S. K. Lin, H. Liu, Y. Li, C. Vargas, R. Luque, *Appl. Catal. A* 2013, *455*, 261–266; e) I. Luz, A. Leon, M. Boronat, F. X. Llabres i Xamena, A. Corma, *Catal. Sci. Technol.* 2013, *3*, 371–379; f) I. Y. Skobelev, A. B. Sorokin, K. A. Kovalenko, V. P. Fedin, O. A. Kholdeeva, *J. Catal.* 2013, *298*, 61–69.
- [14] T. Takai, T. Yamada, T. Mukaiyama, Chem. Lett. 1991, 9, 1499–1502.
- [15] a) B. B. Wentzel, P. L. Alsters, M. C. Feiters, R. J. M. Nolte, J. Org. Chem. 2004, 69, 3453–3464; b) W. W. Nam, H. J. Kim, S. H. Kim, R. Y. N. Ho, J. S. Valentine, Inorg. Chem. 1996, 35, 1045–1049.
- [16] a) H. L. Bao, J. Zhou, Z. Wang, Y. L. Guo, T. P. You, K. L. Ding, *J. Am. Chem. Soc.* 2008, *130*, 10116–10127; b) K. Tanaka, K. Otani, T. Murase, S. Nishihote, Z. Urbanczyk-Lipkowska, *Bull. Chem. Soc. Jpn.* 2012, *85*, 709–714; c) I. Vilotijevic, T. F. Jamison, *Science* 2007, *317*, 1189–1192.
- [17] Y. Fu, D. Sun, M. Qin, R. Huang, Z. Li, RSC Adv. 2012, 2, 3309-3314.
- [18] K. C. Szeto, K. O. Kongshaug, S. Jakobsen, M. Tilset, K. P. Lillerud, Dalton Trans. 2008, 2054–2060.
- [19] A. Gunyar, D. Betz, M. Drees, E. Herdtweck, F. E. Kuhn, J. Mol. Catal. A 2010, 331, 117–124.
- [20] http://cp2k.berlios.de/.
- [21] G. Lippert, J. Hutter, M. Parrinello, Mol. Phys. 1997, 92, 477-487.
- [22] a) S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B* **1996**, *54*, 1703–1710;
 b) C. Hartwigsen, S. Goedecker, J. Hutter, *Phys. Rev. B* **1998**, *58*, 3641–3662.
- [23] C. Adamo, D. Jacquemin, Chem. Soc. Rev. 2013, 42, 845-856.
- [24] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- [25] a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652; b) C. T. Lee, W. T. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.

Received: July 3, 2013 Revised: September 10, 2013 Published online on October 17, 2013