

MOF-Supported Cu Catalyst

Copper-Functionalized Metal–Organic Framework as Catalyst for Oxidant-Controlled Partial Oxidation of Cyclohexene

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Abstract: Microwave irradiation is exploited for the facile, one-step functionalization of Cu(acac)₂ to –NH₂ pendant groups of MIL-53(Al)-NH₂, a metal–organic framework material, under mild reaction conditions and a short reaction time. PXRD, XPS, XAS, and EPR spectroscopy are used to investigate the structure and chemical nature of the copper species on the framework. The copper center exists in the +2 oxidation state with a square-planar geometry and NO₃ coordination environment. The copper complex is anchored to the framework by imine bond formation. This copper-functionalized MIL-53(Al)-NH₂ or

MIL-53[Cu] is employed in the catalytic oxidation of olefins using molecular oxygen (O₂) or *tert*-butyl hydroperoxide (TBHP) as the oxidant. The chemoselectivities of the oxidation products depend on the type of oxidant and substrate. When O₂ is used as the oxidant and isobutyraldehyde as the co-oxidant in the oxidation of cyclohexene with MIL-53[Cu], cyclohexene oxide is the major product. However, when TBHP is employed as the oxidant, 2-cyclohexen-1-one is the major product. Furthermore, the catalyst can be reused at least three times without a significant loss in activity.

Introduction

The oxidation of hydrocarbons is of immense importance to the chemical industry as a means of converting petroleum feedstocks into valuable oxygen-containing compounds.^[1] Many of these oxidation reactions require transition-metal-based catalysts to proceed efficiently and selectively. Transition metals, in the form of homogeneous catalysts, heterogeneous catalysts, and nanoparticles, have been explored for such reactions.^[2] Noble-metal redox couples, such as Pd^{II}/Pd⁰, have been studied in the selective oxidation reactions of alcohols, olefins, and C–H bonds. Copper catalysis seems to be an alternative candidate in these types of reactions, with benefits including lower cost and reduced toxicity, relative to traditional precious-metal catalysts. Moreover, copper-containing enzymes demonstrate their efficacy for oxidation reactions in biotic systems. For these reasons, a number of research groups have turned their attention to the development of abiotic copper catalysts.^[3] The partial oxidation of alkenes has been widely studied with the chal-

lenge to selectively control the type of oxidation products. For example, the copper(II) 2-quinoxalino salen complex exhibits good activity in the homogeneous oxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) to 2-cyclohexen-1-one.^[4] Even though homogeneous catalysts generally provide good catalytic activity and selectivity, the difficulty in product separation and catalyst recyclability is an aspect inferior to that for heterogeneous catalysts. Therefore, to combine the benefits of homogeneous and heterogeneous catalysts, metal complexes, including copper compounds, have been immobilized onto the surfaces of solid supports. A number of copper(II)-complex-anchored mesoporous silicas have been reported as efficient and reusable catalysts for the epoxidation of cyclohexene with TBHP.^[5] Inorganic oxides, such as silica or alumina, are robust and inert to the oxidation reaction; however, the procedure for the installation of tailored active sites on these oxides is rather complicated. Beside inorganic oxides, metal–organic frameworks are another promising class of materials for catalytic support.

Metal–organic frameworks (MOFs) are popular porous hybrid materials composed of organic linkers and inorganic secondary building units to form infinite networks.^[6] Because of their high surface areas and versatile topology, MOFs are emerging materials for applications in gas storage,^[7] sensors,^[8] separation,^[9] drug delivery,^[10] and catalysis.^[7a,11] The MOF structure features prominent characteristics for the design and installation of catalytically active sites. Many researchers have introduced functionalities into MOF lattices through the postsynthetic modification approach.^[12] Metal complexes have also been anchored to the organic linkers of MOF frameworks.^[13] A vanadyl Schiff base complex-functionalized isorecticular MOF was reported as an active catalyst for the oxidation of cyclohexene with TBHP.^[13a]

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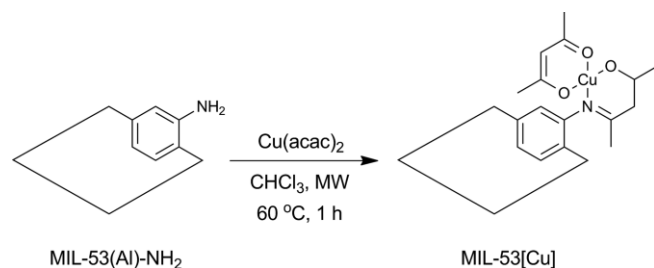
Manganese(II)-complex-functionalized IRMOF-3 was also synthesized and studied in the epoxidation of cyclohexene using trimethylacetaldehyde as a co-oxidant under an oxygen atmosphere.^[13b] However, to functionalize MOFs, long reaction times or multistep reactions are normally required. Recently, microwave-assisted synthesis has become an appealing technique in organic synthesis, because it not only shortens the reaction time, but it also achieves reaction products that conventional heating may not afford.^[14] Therefore, here, microwave-assisted synthesis is exploited to functionalize a MOF with a copper(II) complex in a one-step reaction. MIL-53(Al)-NH₂ or Al(OH)[H₂N-BDC]-guest (BDC = benzene-1,4-dicarboxylate)^[12b] is employed in this study, because of its readily reacting amino groups, as well as its high thermal and chemical stability.

Herein, we describe the facile functionalization of MIL-53(Al)-NH₂ with Cu(acac)₂ by Schiff base condensation using microwave-assisted one-step synthesis. The copper-functionalized product (MIL-53[Cu]) is investigated as a heterogeneous catalyst for the partial oxidation of cyclohexene. The catalytic reaction is scrutinized and the selectivity of the product can be carefully controlled by the type of oxidant. In addition, other olefinic substrates, such as cyclooctene, norbornene, *trans*-stilbene, styrene, and 1-octene, are also examined.

Results and Discussion

Characterization of MIL-53[Cu]

Although microwave heating has been widely employed to synthesize MOFs,^[15] including MIL-53(Al)-NH₂,^[16] it has not been utilized much in the functionalization step. In this study, copper(II)-functionalized MIL-53 or MIL-53[Cu] was successfully synthesized by microwave-assisted one-step synthesis. As illustrated in Scheme 1, the amino groups on the MIL-53(Al)-NH₂ framework react with Cu(acac)₂ by Schiff base condensation under microwave irradiation at 60 °C for 1 h to afford MIL-53[Cu]. The monoclinic structure of the metal-organic framework is retained after the functionalization (Figure 1). However, the peaks are broader, indicating the smaller crystallite size of MIL-53[Cu], compared with that of the parent MOF. A slight shift can also be observed for all peaks, except the ones corresponding to the planes perpendicular to the pores (*hkl* = 200 and 400). The shift is probably caused by changes to the pore geometry, as a result of the introduction of the copper complex inside the pores.^[17]



Scheme 1. Preparation of MIL-53[Cu].

To confirm successful functionalization, the X-ray photoelectron spectroscopy (XPS) technique was employed to evaluate

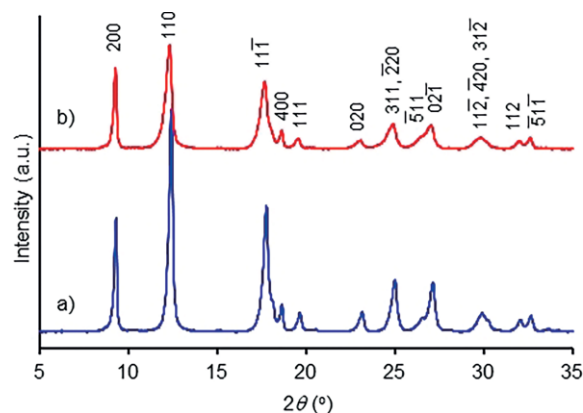


Figure 1. Powder X-ray diffraction (XRD) patterns of: (a) MIL-53(Al)-NH₂; and (b) MIL-53[Cu].

the surface composition and functionality. The high-resolution XPS analysis reveals a copper content of 1.96 wt.-%, which is higher than the value obtained from the inductively coupled plasma optical-emission spectroscopy (ICP-OES) measurement (0.86 wt.-%). Therefore, the surface of the functionalized material is copper-rich, in comparison with the bulk, and the copper complex is located preferentially at the external surface. The XPS spectra of MIL-53(Al)-NH₂ and MIL-53[Cu] are displayed in Figure 2. Only the MIL-53[Cu] sample provides signals, with binding energies of 934.9 and 954.9 eV for Cu 2p_{3/2} and Cu 2p_{1/2}, respectively.^[18] These peaks are characteristic of copper(II) species, confirming the oxidation state of copper in the functionalized sample. The N 1s spectrum of MIL-53(Al)-NH₂ exhibits only one symmetrical peak, with a binding energy of 399.6 eV, which is attributed to the nitrogen atom of the amino pendant groups on the organic linker of the framework.^[18c,19] In contrast, the N 1s spectrum of MIL-53[Cu] shows an unsymmetrically shaped band that can be deconvoluted into two peaks, with binding energies of 399.6 and 400.9 eV. The former peak corresponds to the amino group at the same binding energy as that found in the parent MOF, thus providing evidence that not all amino pendant groups reacted with Cu(acac)₂. The latter peak is assigned to the nitrogen atom of the imine functionality^[18c] from Schiff base condensation between the amino group of the parent framework and the carbonyl group of Cu(acac)₂. The C 1s spectra of both MIL-53(Al)-NH₂ and MIL-53[Cu] are deconvoluted into a number of peaks. The peaks at 284.9 and 286.1 eV are attributed to the aryl carbon and the aryl carbon adjacent to carboxylate group, respectively, while the peaks at 287.8, 289.1, and 290.8 eV are assigned to the carbon atoms attached to different oxygen-containing moieties.^[18b,20] The binding energies of the carbon atoms bonded to nitrogen was expected to be in the range of 286–288 eV,^[18b,20c] which is not clearly observed here, perhaps due to the relatively low content of carbon–nitrogen bonds and the stronger signals from carbon–oxygen moieties.

The electron paramagnetic resonance (EPR) spectrum of MIL-53[Cu] exhibits a four-line isotropic pattern of mononuclear copper(II) species with $g_{||} = 2.31$, $g_{\perp} = 2.07$, and $A_{||} = 444$ MHz (Figure 3). With $g_{||} > g_{\perp} > 2.0023$, the parameters are characteristic of a copper(II) ion whose unpaired electron occupies the

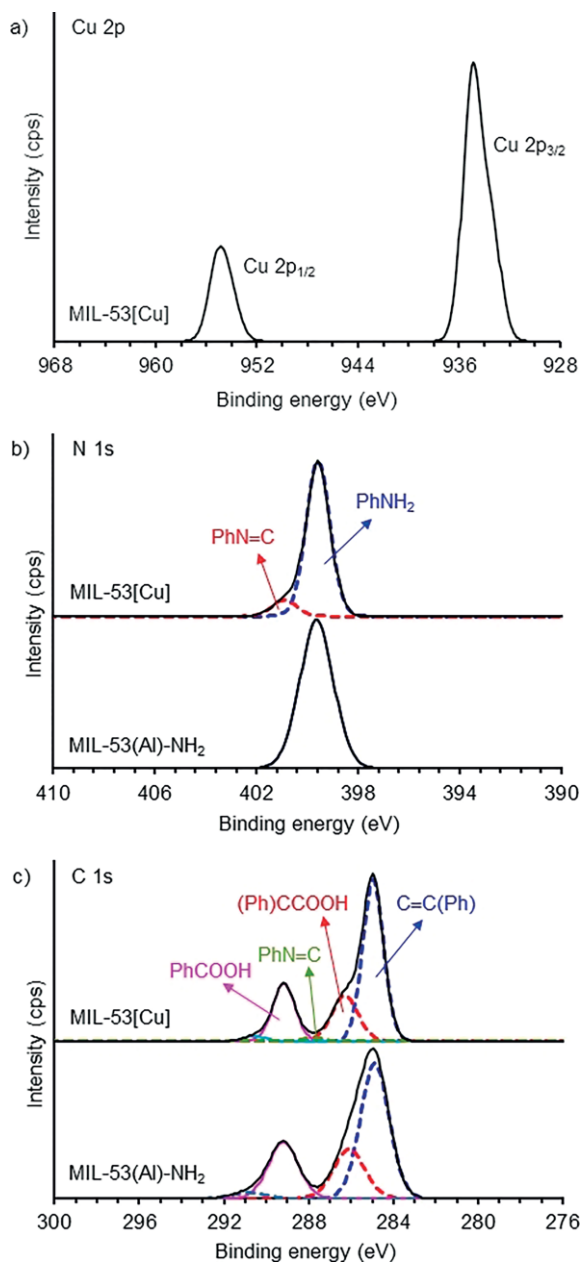


Figure 2. XPS spectra of MIL-53(Al)-NH₂ and MIL-53[Cu] in the regions: (a) Cu 2p; (b) N 1s; and (c) C 1s.

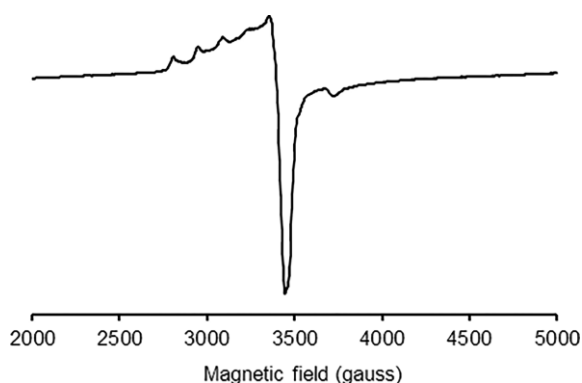


Figure 3. EPR spectrum of MIL-53[Cu].

$d_{x^2-y^2}$ orbital in a tetrahedrally elongated or square-planar geometry.^[21] Furthermore, both the g_{\parallel} and A_{\parallel} values closely agreed with those reported for copper(II) complexes with an equatorial NO₃ coordination.^[22]

The structure around the copper in MIL-53[Cu] was also investigated by X-ray absorption near-edge-structure (XANES) spectroscopy. The Cu K-edge XANES spectra of MIL-53[Cu] and CuO are compared in Figure 4. The absence of the pre-edge signal indicates that the copper ion has approximately square-planar geometry.^[23] In addition, the edge energy of 8987.5 eV for MIL-53[Cu] confirms the presence of copper(II) species.^[24] These results, along with the XPS and EPR studies, suggest that the coordination environment of the copper(II) center in MIL-53[Cu] should be as depicted in Scheme 1.

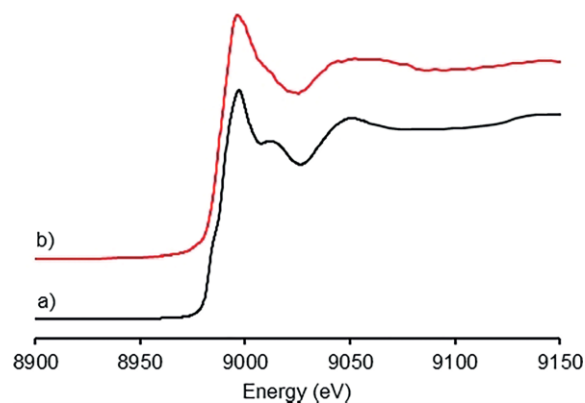
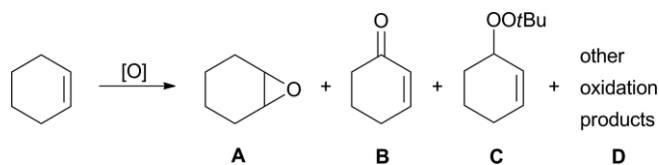


Figure 4. Cu K-edge XANES spectra of: (a) CuO; and (b) MIL-53[Cu].

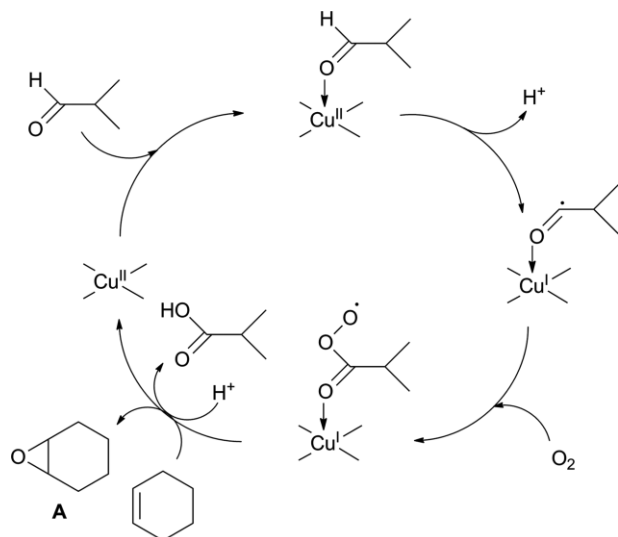
Catalytic Oxidation of Cyclohexene by MIL-53[Cu] using Molecular Oxygen as the Oxidant

Catalytic oxidation of cyclohexene (Scheme 2) is a good model to investigate whether a catalytic system prefers epoxidation or allylic oxidation. When MIL-53[Cu] was used as a catalyst for the aerobic oxidation of cyclohexene, with isobutyraldehyde as a co-oxidant, cyclohexene oxide (**A**) was the major product. Thus, the epoxidation predominates for this catalytic system. The mechanism for the epoxidation of alkenes with molecular oxygen and aldehyde co-oxidant has been well proposed in the literature.^[25] For MIL-53[Cu], the copper(II) center will bind to isobutyraldehyde, followed by the formation of copper-bound acyl radical, as illustrated in Scheme 3. After reaction with O₂, a copper-acylperoxy intermediate is formed, and subsequently, the epoxidation of cyclohexene by the acylperoxy radical occurs to yield cyclohexene oxide, as well as to regenerate the copper(II) catalyst. Therefore, the major role of the metal catalyst is to stabilize the acylperoxy radical and to enhance the selectivity to epoxide. In our study, this mechanism was further supported by the detection of isobutyric acid by gas chromatography mass spectrometry (GCMS).

To ensure that molecular oxygen was the oxidant for the reaction, the oxidation of cyclohexene was carried out under different atmospheric gases; the results are summarized in Table 1 (entries 1–3). Under an argon atmosphere, the reaction does not proceed at all, while moderate conversion is observed



Scheme 2. Oxidation of cyclohexene.



Scheme 3. Proposed mechanism for epoxidation of cyclohexene catalyzed by MIL-53[Cu] using molecular oxygen as the oxidant and isobutyraldehyde as the co-oxidant.

under air. Using the same reaction conditions, almost complete conversion of cyclohexene is achieved under an oxygen atmosphere. These results imply that the reaction requires an excess amount of oxygen to generate the acylperoxy radical as the active oxidizing species. In addition, to verify the proposed mechanism in Scheme 3, a radical scavenger, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), was added to the reaction (Table 1, entry 4). As a result, the reaction loses all conversion and no product is observed, indicating that the reaction proceeds according to the radical mechanism. In the absence of isobutyraldehyde, the reaction also fails to generate any oxidation products (Table 1, entry 5). Therefore, the oxidation of cyclohexene to cyclohexene oxide by MIL-53[Cu] requires both molecular oxygen and isobutyraldehyde.

Table 1. Oxidation of cyclohexene catalyzed by MIL-53[Cu].^[a]

Entry	Atmosphere	Conversion [%]	Selectivity [%]	
			A	B
1	Ar	< 1		
2	air	37	89	11
3	O ₂	99	94	6
4 ^[b]	O ₂	< 1		
5 ^[c]	O ₂	< 1		

[a] Reaction conditions: MIL-53[Cu] (5 wt-%), cyclohexene (2.4 mmol), isobutyraldehyde (7.2 mmol), gas (1 bar), CH₃CN (24 mL), 50 °C, 3 h. [b] In the presence of 10 mol-% TEMPO. [c] In the absence of isobutyraldehyde.

Table 2 lists the solvents that were examined for the oxidation of cyclohexene catalyzed by MIL-53[Cu], with molecular

oxygen as the oxidant and isobutyraldehyde as the co-oxidant. The reaction in polar aprotic solvents, such as CH₃CN and 1,2-dichloroethane, performs superiorly to others, with excellent conversion and good selectivity for epoxide. Nonpolar solvents exhibit excellent selectivity, but the conversions are not as good. Highly polar solvents can stabilize highly polar intermediate species more efficiently than mildly polar solvents. However, the coordinating ability of EtOH towards copper^[26] may lead to the blockage of the active copper center from isobutyraldehyde and cause a drastic decrease in the conversion of cyclohexene. Moreover, 2-cyclohexen-1-one is produced as a minor product, indicating that allylic oxidation also occurs. During the epoxidation, the carboxyl radical is generated in addition to isobutyric acid. This carboxyl radical can decompose to carbon dioxide and alkyl radical, which then reacts with O₂ to form alkyl peroxy radical as the active species for the allylic oxidation.^[25d]

Table 2. Oxidation of cyclohexene catalyzed by MIL-53[Cu] using molecular oxygen as the oxidant and isobutyraldehyde as the co-oxidant in various solvents.^[a]

Entry	Solvent	Conversion [%]	Selectivity [%]	
			A	B
1	CH ₃ CN	97	87	13
2	1,2-dichloroethane	100	90	10
3	EtOAc	90	90	10
4	benzene	73	96	4
5	toluene	31	96	4
6	<i>n</i> -heptane	28	95	5
7	EtOH	< 1		

[a] Reaction conditions: MIL-53[Cu] (5 wt-%); cyclohexene (2.4 mmol); isobutyraldehyde (7.2 mmol); O₂ (2 bar); solvent (24 mL); 50 °C; 24 h.

In addition to the nature of the solvents, the aldehyde-to-substrate ratio can affect the oxidation activity of the catalyst. As shown in Table 3, entries 1–3, when the ratio is increased from 1 to 5, both the conversion of cyclohexene and the selectivity to epoxide increase. Even though the proposed mechanism in Scheme 3 only requires one equivalent of isobutyraldehyde, these results agree well with the previous studies.^[25b,25d] Wentzel et al. found that if the aldehyde-to-substrate ratio is less than two, the reaction proceeds very slowly and only a small amount of epoxide is formed. When the ratio is greater than two, the epoxidation is first-order dependent on the aldehyde.^[25d] However, the cause of this phenomenon is not clear.

Table 3. Oxidation of cyclohexene catalyzed by MIL-53[Cu] using molecular oxygen as the oxidant and isobutyraldehyde as the co-oxidant at different aldehyde/substrate ratio and temperature.^[a]

Entry	Aldehyde/substrate ratio	Temp. [°C]	Conversion [%]	Selectivity [%]		
				A	B	D ^[b]
1	1	50	11	80	20	
2	3	50	53	94	6	
3	5	50	63	93	7	
4	3	30	10	91	9	
5	3	70	76	88	10	2

[a] Reaction conditions: MIL-53[Cu] (5 wt-%); cyclohexene (2.4 mmol); isobutyraldehyde; O₂ (1 bar); CH₃CN (24 mL); 1 h. [b] 7-Oxabicyclo [4.1.0]heptan-2-one.

The reaction temperature can affect the oxidation of cyclohexene too. As demonstrated in Table 3, entries 2, 4, and 5,

higher conversion can be achieved at higher temperatures. Nevertheless, at the reaction temperature of 70 °C, the selectivity for the epoxide product slightly decreases and an over-oxidation product, 7-oxabicyclo[4.1.0]heptan-2-one, is observed. The effect of the amount of MIL-53[Cu] catalyst on the oxidation of cyclohexene is reported in Table 4, entries 1–4. Generally, higher catalyst loading leads to higher conversion, but the selectivity is not significantly affected. Furthermore, the conversion of cyclohexene increases with the reaction time (Table 4, entries 3, 5, and 8). A conversion of 99 % is reached within 3 h and the selectivity for the epoxide is 94 %, with 2-cyclohexen-1-one as the other product. At longer reaction times, a small amount of 7-oxabicyclo[4.1.0]heptan-2-one is detected, while the selectivity for epoxide is not significantly changed. To demonstrate the catalytic enhancement due to the presence of the copper complex, the parent MIL-53(Al)-NH₂ was also tested as a catalyst under the same reaction conditions. The results show that the presence of the copper complex in MIL-53[Cu] improves the conversion (Table 4, entries 3 versus 9), even though the selectivity remains similar.

Table 4. Oxidation of cyclohexene catalyzed by MIL-53[Cu] using molecular oxygen as the oxidant and isobutyraldehyde as the co-oxidant at different catalyst loading and reaction times.^[a]

Entry	Catalyst loading [wt.-%]	Time [h]	Conversion [%]	Selectivity [%]		
				A	B	D ^[b]
1	1	1	36	92	8	
2	3	1	45	92	8	
3	5	1	53	94	6	
4	7	1	55	92	8	
5	5	3	99	94	6	
6 ^[c]	5	3	100	90	6	4
7 ^[d]	5	3	99	87	7	6
8	5	5	100	93	6	1
9 ^[e]	5	1	26	98	2	

[a] Reaction conditions: MIL-53[Cu], cyclohexene (2.4 mmol); isobutyraldehyde (7.2 mmol); O₂ (1 bar); CH₃CN (24 mL); 50 °C. [b] 7-Oxabicyclo[4.1.0]heptan-2-one. [c] The catalyst recovered from entry 5 was used. [d] The catalyst recovered from entry 6 was used. [e] MIL-53(Al)-NH₂ was used as a catalyst.

To study its reusability, the MIL-53[Cu] catalyst was recovered from the oxidation reaction, washed with CH₂Cl₂ (3 × 5 mL), and dried at 80 °C overnight before being used in the next catalytic run. The catalyst successfully catalyzes the oxidation of cyclohexene in three consecutive runs, without a loss of activity

(Table 4, entries 5–7). According to the XRD experiments (Figure 5), the crystallinity of the recovered catalyst was poorer, and the crystal structure changed from monoclinic to orthorhombic symmetry, which is a common phenomenon for the MIL-53 family when guest species enter its pores.^[12b] Among the results for the catalytic oxidation of cyclohexene in the presence of molecular oxygen and isobutyraldehyde, the best conditions to carry out the reaction are at 50 °C for 3 h using MIL-53[Cu] (5 wt.-% loading with respect to the mass of cyclohexene in CH₃CN) and isobutyraldehyde (3 equiv.) under O₂ (1 bar). The reaction achieves 99 % conversion of cyclohexene and 94 % selectivity for cyclohexene oxide.

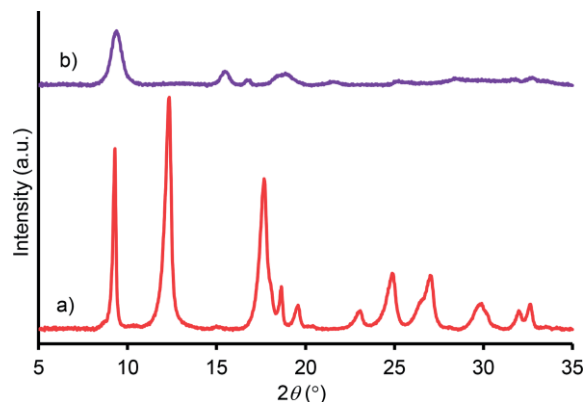


Figure 5. XRD patterns of MIL-53[Cu] catalyst: (a) fresh; and (b) after being used.

Table 5 shows the comparison of the performance in the oxidation of cyclohexene of MIL-53[Cu] with Cu(acac)₂ and other copper catalysts in the literature.^[27,28] Even though it is difficult to directly compare the results, due to the different reaction conditions, in general, our catalyst seems to provide higher conversion with excellent selectivity in a much shorter reaction time. In terms of turnover frequency, the copper Schiff base complex-immobilized MCM-41 [Cu-AM(PS)] provides good TOF, but still lower selectivity for epoxide. In addition, MIL-53[Cu] exhibits superior performance to the analogous homogeneous catalyst, Cu(acac)₂, when the copper contents in both catalysts are equal. Thus, MIL-53[Cu] is an effective catalyst for the epoxidation of cyclohexene.

The oxidation of other olefins by MIL-53[Cu] in the presence of oxygen and isobutyraldehyde were also investigated, as

Table 5. Oxidation of cyclohexene using oxygen as the oxidant and isobutyraldehyde as the co-oxidant catalyzed by various catalysts.

Catalyst	Reaction condition	Conv. [%]	Selectivity for epoxide [%]	TOF ^[a] [h ⁻¹]	Ref.
MIL-53[Cu]	0.01 g catalyst, 2.4 mmol cyclohexene, CH ₃ CN, 50 °C, 3 h	99	94	585	this work
Cu-AM(PS)	0.05 g catalyst, 5 mmol cyclohexene, CH ₃ CN, 40 °C, 8 h	80	77	316	[27]
Cu ²⁺ @COMOC-4	0.19 g catalyst, 5 mmol cyclohexene, CHCl ₃ , 40 °C, 7 h	49	89	21.5	[28]
Cu-BTC	0.19 g catalyst, 5 mmol cyclohexene, CHCl ₃ , 40 °C, 7 h	42	78	11.1	[28]
Cu(acac) ₂	0.35 mg catalyst, 2.4 mmol cyclohexene, CH ₃ CN, 50 °C, 1 h	28	92	506	this work

[a] TOF: turnover frequency = mol of substrates converted per mol of metal center per hour.

shown in Table 6. For cyclooctene, norbornene, and *trans*-stilbene, the conversions are almost complete with excellent selectivity for epoxide. For styrene, the oxidation is more cumbersome and a considerable amount of benzaldehyde is obtained. The oxidation of 1-octene is slower, with 48 and 73 % conversion at 3 and 24 h, respectively, but 99 % selectivity for epoxide was realized for both reaction times. These results suggest that the catalytic system performs efficient epoxidation with several types of olefins. Therefore, overall, this catalytic system is versatile for the epoxidation of olefins, especially cyclic and internal olefinic substrates.

Table 6. Oxidation of different olefins by MIL-53[Cu] using oxygen as the oxidant and isobutyraldehyde as the co-oxidant.^[a]

Entry	Substrate	Conv. [%]	Selectivity [%]		
			Epoxide	Ketone	Others
1 ^[b]	cyclooctene	99	> 99	< 1	
2	norbonene	> 99	100		
3	<i>trans</i> -stilbene	> 99	97		3 ^[c]
4 ^[d]	styrene	13	68		32 ^[c]
5	1-octene	48	99	1	
6 ^[e]	1-octene	73	99	1	

[a] Reaction conditions: MIL-53[Cu] (5 wt.-%); alkene (2.4 mmol); isobutyraldehyde (7.2 mmol); O₂ (1 bar); CH₃CN (24 mL); 50 °C; 3 h. [b] Using 1,2-dichloroethane as solvent. [c] Benzaldehyde. [d] Reaction time: 6 h. [e] Reaction time: 24 h.

Catalytic Oxidation of Cyclohexene by MIL-53[Cu] using *tert*-Butyl Hydroperoxide (TBHP) as the Oxidant

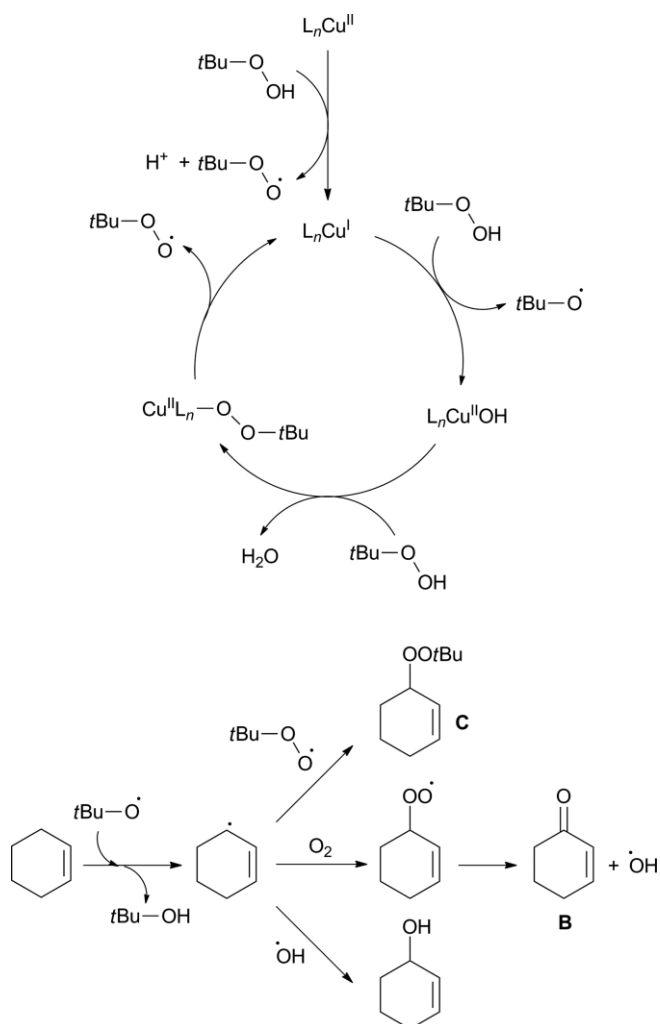
The selectivity of oxidation products is controlled not only by the active site of the catalyst, but also by the type of oxidant. In our study, the catalytic oxidation of olefins by MIL-53[Cu] catalyst, using oxygen as the oxidant and isobutyraldehyde as the co-oxidant, provides epoxides as the major products. To obtain other oxidation products, TBHP was chosen as the oxidant, because there are previous reports suggesting that allylic oxidation can occur when TBHP is used in the copper-catalyzed oxidation of cyclohexene.^[29] Table 7 presents the catalytic cyclohexene oxidation, using MIL-53[Cu] as the catalyst and TBHP as the oxidant, under different reaction atmospheres. Under these conditions, the allylic oxidation dominates; the mechanism is depicted in Scheme 4. The MIL-53[Cu] catalyst initiates the reaction by reacting with TBHP to generate active radical species for the oxidation of cyclohexene. Under an argon atmosphere, *tert*-butyl-2-cyclohexenyl-1-peroxide (**C**) is obtained as the major product (Table 7, entry 1). According to the mechanism, the allylic H-abstraction of cyclohexene produces a cyclohexenyl radical, which then reacts with *tert*-butyl peroxide radical to afford this peroxide product.^[2d,30] The peroxide will subsequently decompose to 2-cyclohexen-1-one, but this process is quite slow.^[30b] Therefore, the peroxide was the major product for the oxidation under an inert atmosphere. The selectivity for 2-cyclohexen-1-one (**B**) increases when the reaction is carried out under air (Table 7, entry 2) because the oxygen in the air can react with the cyclohexenyl radical to yield the ketone product.^[4] Furthermore, 2-cyclohexen-1-one is the major product for the reaction under an oxygen atmosphere

(Table 7, entry 4) and overoxidation products, such as 2-cyclohexene-1,4-dione and 7-oxabicyclo[4.1.0] heptan-2-one, are observed as well. This result implies that, with excess oxygen, the rate of the reaction between the cyclohexenyl radical and oxygen is faster than that of the cyclohexenyl radical and the *tert*-

Table 7. Oxidation of cyclohexene by MIL-53[Cu] using TBHP as the oxidant under different reaction atmosphere.^[a]

Entry	Atmosphere	Pressure [bar]	Conversion [%]	Selectivity [%]			
				A	B	C	E ^[b]
1	Ar	1	75	< 1	7	91	1
2	air	1	59	< 1	28	64	7
3 ^[c]	air	1	87	1	31	66	2
4	O ₂	1	71	4	81	1	14
5 ^[d]	O ₂	1	< 1				
6 ^[c]	O ₂	1	91	5	70	2	23
7	O ₂	2	79	3	69	2	26
8	O ₂	4	78	3	68	1	28

[a] Reaction conditions: MIL-53[Cu] (5 wt.-%); cyclohexene (2.4 mmol); TBHP (7.2 mmol); CH₃CN (24 mL); 50 °C; 24 h. [b] A mixture of 2-cyclohexen-1-ol, 2-cyclohexene-1,4-dione, and 7-oxabicyclo[4.1.0]heptan-2-one. [c] Reaction temperature: 70 °C. [d] In the presence of Ph₂NH (50 mol-%).



Scheme 4. Proposed mechanism for allylic oxidation of cyclohexene catalyzed by MIL-53[Cu] using TBHP as the oxidant.

butyl peroxide radical. To confirm the proposed mechanism in Scheme 4, an oxygen-radical scavenger, diphenylamine, was added to the reaction (Table 7, entry 5). As a result, the reaction did not occur, indicating that the reaction proceeds according to the radical mechanism.

Raising the reaction temperature from 50 to 70 °C increases the conversions under both air and an oxygen atmosphere (Table 7, entries 3 and 6). However, under oxygen, the selectivity to 2-cyclohexen-1-one declines, due to the appearance of overoxidation products. Similarly, if the pressure of oxygen is increased, higher conversion of cyclohexene is obtained with more production of overoxidation products (Table 7, entries 4, 7, and 8).

In this study, we have demonstrated that the selectivity can be finely tuned by changing the atmospheric gas. Under oxygen, the catalytic oxidation of cyclohexene by MIL-53[Cu], using TBHP as the oxidant, affords ketone as the major product. Whereas, under air, the reaction generates peroxide as the major product, which is the common product reported for late-transition-metal-catalyzed cyclohexene oxidation.^[31] In addition, the reaction in the absence of TBHP does not yield any oxidation products, indicating that the catalyst cannot activate molecular oxygen directly under these conditions. The oxidation of cyclohexene, using TBHP as the oxidant, under an oxygen atmosphere, was further explored. According to the reaction mechanism shown in Scheme 4, TBHP can be activated by the catalyst to generate active radicals. However, it is also known that TBHP can just decompose during the reaction.^[4] Therefore, the amount of TBHP is an important parameter to study. The molar ratio of TBHP to cyclohexene was varied from 1 to 5 and the results are summarized in Table 8. Higher conversion is attained when the amount of TBHP is increased (Table 8, entries 1–3). However, when the molar ratio of TBHP to cyclohexene is equal to 5, the selectivity for 2-cyclohexen-1-one is decreased and overoxidation products are observed. In addition, with other parameters kept constant, when the reaction time is reduced from 24 to 6 h, the conversion and selectivity profiles remain comparable (Table 8, entries 3–4). Nevertheless, further reduction of the reaction time to 2 h leads to a decrease in the conversion (Table 8, entry 5). Catalyst loading can also

contribute to the reaction activity. The conversion of cyclohexene is increased with increasing amount of the catalyst (Table 8, entries 4, 6–8) and it reaches the highest at 5 wt.-% loading of MIL-53[Cu], with respect to the mass of cyclohexene. If MIL-53(Al)-NH₂ is used as a catalyst, in place of MIL-53[Cu] (Table 8, entries 2 versus 11), lower conversion is obtained, with a similar product distribution. Thus, the incorporation of the copper complex can increase the catalytic activity, possibly by facilitating the formation of active radicals.

In addition, to study its reusability, the MIL-53[Cu] catalyst was recovered from the oxidation reaction, washed with CH₂Cl₂ (3 × 5 mL), and dried at 80 °C overnight before being used in the next catalytic run. The catalyst successfully catalyzes the oxidation of cyclohexene in three consecutive runs, with similar activity (Table 8, entries 4, 9–10). According to the XRD experiments (Figure 6), the recovered catalyst remains crystalline, and the crystal structure in the monoclinic symmetry is preserved. A small quantity of copper ($\delta = 0.5$ ppm) is detected in the reaction medium after the catalytic reaction that may be responsible for the slight drop of conversion in the third run. We did not recycle the catalyst any further, because the small scale of the experiment led to difficulty in the recovery of catalyst particles after the third run.

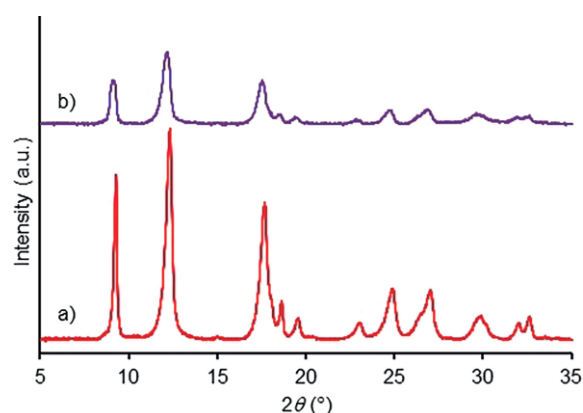


Figure 6. XRD patterns of MIL-53[Cu] catalyst: (a) fresh; and (b) after being used.

Table 8. Oxidation of cyclohexene by MIL-53[Cu] using TBHP as the oxidant under an oxygen atmosphere.^[a]

Entry	TBHP/substrate ratio	Time [h]	Catalyst. loading [wt.-%]	Conversion. [%]	Selectivity [%]			
					A	B	C	E ^[b]
1	1	24	5	50	3	76	< 1	20
2	3	24	5	71	4	81	1	14
3	5	24	5	87	2	69	2	27
4	3	6	5	75	3	73	4	20
5	3	2	5	51	2	67	6	25
6	3	6	10	70	2	72	3	23
7	3	6	3	61	3	82	2	13
8	3	6	1	58	2	72	2	24
9 ^[c]	3	6	5	75	2	70	2	26
10 ^[d]	3	6	5	71	3	67	2	28
11 ^[e]	3	24	5	48	1	73	2	24

[a] Reaction conditions: MIL-53[Cu]; cyclohexene (2.4 mmol); TBHP, CH₃CN (24 mL); 50 °C. [b] A mixture of 2-cyclohexen-1-ol, 2-cyclohexene-1,4-dione, and 7-oxabicyclo[4.1.0]heptan-2-one. [c] The catalyst recovered from entry 4 was used. [d] The catalyst recovered from entry 9 was used. [e] MIL-53(Al)-NH₂ was used as a catalyst.

Table 9. Oxidation of cyclohexene with TBHP catalyzed by various catalysts.

Catalyst	Reaction conditions	Conversion [%]	Selectivity for ketone [%]	TOF ^[a] [h ⁻¹]	Ref.
MIL-53[Cu]	0.01 g catalyst, 2.4 mmol cyclohexene, 7.2 mmol TBHP CH ₃ CN, 50 °C, 6 h	75	73	222	this work
[Cu ₂ (bipy) ₂ (btec)] _∞	0.05 g catalyst, 40 mmol cyclohexene, 40 mmol TBHP DCE, 75 °C, 6 h	33	72	22	[29a]
Cu-amp-AMPS	0.1 g catalyst, 5.5 mmol cyclohexene, CH ₃ CN, 50 °C, 10 h	79	74	18.2	[29b]
PS-NH ₂ -Cu-Sal	0.05 g catalyst, 5 mmol cyclohexene, 10 mmol TBHP, CH ₃ CN, 50 °C, 7 h	74	66	17.6	[29c]
Cu(acac) ₂	0.35 mg catalyst, 2.4 mmol cyclohexene, 7.2 mmol TBHP CH ₃ CN, 50 °C, 24 h	54	71	40.7	this work

[a] TOF: turnover frequency = mol of substrates converted per mol of metal center per hour.

Among the conditions tested, the most efficient one for the oxidation of cyclohexene to 2-cyclohexene-1-one is to use MIL-53[Cu] (5 wt.-%) as the catalyst with TBHP (3 equiv.) under oxygen (1 bar) at 50 °C. After 6 h of reaction, the conversion reaches 75 % with 73 % selectivity. The performance of MIL-53[Cu] catalyst is compared with other heterogeneous copper catalysts,^[29] as illustrated in Table 9. MIL-53[Cu] can achieve comparable or higher conversion and selectivity at a shorter reaction times. In addition, the activity, in terms of the TOF, is higher than the others, including the homogeneous analogous Cu(acac)₂ catalyst. The confined space in the MOF may assist the catalytic oxidation of cyclohexene, resulting in the excellent performance of MIL-53[Cu]. Thus, MIL-53[Cu] has high potential for application as a catalyst in the oxidation of cyclohexene with TBHP. The oxidation of other olefins by the MIL-53[Cu] catalyst, using TBHP as an oxidant, under an oxygen atmosphere, were also studied, as shown in Table 10. The catalytic oxidation of cyclooctene exhibits moderate conversion of 43 %, with cyclooctene oxide as the major product. In contrast to cyclohexene, the allylic oxidation is less favorable for cyclooctene, because for the predominant conformation of cyclooctene, the σ_{C-H} orbital at the allylic position is nearly orthogonal to the $\pi_{C=C}$ orbital, resulting in poor overlap.^[32] Thus, the allylic H-abstraction is disfavored. The oxidation of norbornene reveals excellent conversion and selectivity for norbornene oxide. Even though allylic hydrogen atoms are available, the allylic oxidation does not proceed, because the allylic H-abstraction of norbornene would produce an unstable bridgehead radical.^[33] As a result, only epoxidation occurs and norbornene oxide is the only product. In the case of a substrate without allylic hydrogen, such as *trans*-stilbene, stilbene oxide is formed as the major product and benzaldehyde is also produced as the minor product, due to oxidative cleavage of the double bond in *trans*-stilbene.^[34] For styrene, the oxidation occurs quite fast and the epoxidation dominates. However, the styrene oxide product is further converted to benzaldehyde. As a result, in the case of styrene, the selectivity for epoxide is not good. For 1-octene, an aliphatic alkene, a low conversion of 10 % is achieved, with 54 and 46 % selectivity for the epoxide and ketone products, respectively, indicating that allylic oxidation and epoxidation of 1-octene proceed with a similar rate. Therefore, the type of olefinic substrate plays a very important role in dictating the selectivity for products in the oxidation of olefins by MIL-53[Cu], using TBHP as the oxidant.

Table 10. Oxidation of different olefins by MIL-53[Cu] using TBHP as the oxidant under an oxygen atmosphere.^[a]

Entry	Substrate	Conversion [%]	Selectivity [%]		
			Epoxide	Ketone	Others
1	cyclooctene	43	77	23	
2	norbornene	56	100		
3	<i>trans</i> -stilbene	60	73		27 ^[b]
4 ^[c]	styrene	75	51		49 ^[b]
5	1-octene	10	54	46	

[a] Reaction conditions: MIL-53[Cu] (5 wt.-%); alkene (2.4 mmol); TBHP (7.2 mmol); CH₃CN (24 mL); 70 °C; 24 h. [b] Benzaldehyde. [c] Reaction time: 6 h.

Conclusion

MIL-53[Cu], a copper-complex-functionalized MIL-53(Al)-NH₂ catalyst, was prepared by a microwave-assisted one-step post-synthetic modification through Schiff base condensation of the amino groups on a MOF framework and the carbonyl moiety of the acetylacetonate ligand of the copper precursor. The MOF crystal structure remained intact after the functionalization. XPS spectra in the N 1s region confirmed the imine bond formation; EPR and XANES analyses suggested that the copper center is in a +2 oxidation state, with a square-planar geometry and an NO₃ coordination environment. Therefore, the copper(II) Schiff base complex was successfully embedded in the MIL-53 framework. MIL-53[Cu] is an active catalyst for the oxidation of cyclohexene. The selectivity for the oxidation product depends on the type of oxidant, as well as the reaction conditions. When oxygen was used as the oxidant and isobutyraldehyde as the co-oxidant, cyclohexene oxide was the major product, with 94 % selectivity at 99 % conversion of cyclohexene. However, when TBHP was employed as the oxidant under an oxygen atmosphere, 2-cyclohexen-1-one was the major product, with 73 % selectivity at 75 % conversion. Thus, MIL-53[Cu] is potentially useful as a heterogeneous catalyst for the oxidation of olefins.

Experimental Section

Materials: AlCl₃·6H₂O (≥ 99 %) was obtained from Merck, while 2-aminoterephthalic acid (H₂N-H₂BDC, ≥ 98 %), *tert*-butyl hydroperoxide (TBHP) solution in decane (5.5 M), and *n*-nonane (99 %) were received from Aldrich. Cu(acac)₂ (98 %), isobutyraldehyde (99 %), and cyclohexene (99 %) were purchased from Acros Organics. Cy-

clooctene (95 %), norbonene (95 %), *trans*-stilbene (96 %), styrene (99 %), and 1-octene (98 %) were obtained from TCI, Fluka, Merck, and Aldrich, respectively. Deionized water, used in all experiments, was obtained from a Nanopure® Analytical Deionization Water System with an electronic resistance of $\geq 18.2 \Omega$. All other solvents were analytical (AR) grade and were purchased from RCI Labscan.

Preparation of MIL-53(Al)-NH₂ and MIL-53[Cu]

The preparation of MIL-53(Al)-NH₂ was adapted from the literature.^[12b] H₂N-H₂BDC (0.24 g) was dispersed in water (56 mL) in a Teflon™ cup. Then, NaOH (1.12 mL, 0.4 M) and AlCl₃·6H₂O (2.2 mL, 0.4 M) were added. The Teflon™ cup was sealed in a stainless-steel reactor that was placed in an oven at 110 °C for 48 h. After that, the resulting product was isolated by filtration and washed with water. This as-synthesized product was then activated in DMF at 130 °C for 18 h. Finally, pale-yellow powder was obtained after filtration and was dried at 130 °C overnight.

Copper-functionalized MIL-53 or MIL-53[Cu] was prepared by microwave-assisted one-step synthesis. In a microwave reaction vessel, MIL-53(Al)-NH₂ (0.1 g) was added to solution of Cu(acac)₂ (5 mL, 0.089 g, 0.34 mmol) in CHCl₃. The vessel was placed in the microwave reactor (CEM, Discover S) and heated to 60 °C, at 2 bar and 100 W for 1 h. The solid product was filtered out, washed with CHCl₃ (5 × 10 mL), and dried at 80 °C overnight to afford the light-green powder of MIL-53[Cu] (0.0724 g).

Characterization: XRD data were collected with a Bruker D8 Advance diffractometer using Cu-K α radiation with a Ge crystal and Johansson type monochromator ($\lambda = 1.540619 \text{ \AA}$); the measurements were conducted at 40 kV and 40 mA, with a step size of 0.075° and a counting time of 1 s/step. EPR spectra were collected with a Bruker e500 spectrometer at room temperature, with a frequency of 9.86 GHz and microwave power of 2.02 W. Copper content in the samples was analyzed by ICP-OES (Spectro CIROSCCD), with an emission line at 324.754 nm. XPS measurements were carried out with an AXIS ULTRADLD instrument equipped with a monochromated 150 W Al-K α ; binding-energy (BE) values were obtained by curve fitting and were referenced to the C 1s band at 284.6 eV. X-ray absorption spectroscopy (XAS) studies were carried out at Beamline-8 of the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand.^[35] The storage ring was operated at 1.2 GeV, with a beam current of 80–150 mA. The energy was calibrated by using copper foil as a reference at 8979 eV before XAS data were collected. The experiments were conducted at room temperature in the fluorescence mode, with a 13-element germanium detector (Canberra). The synchrotron beam was monochromated using a Ge(220) double-crystal monochromator with an energy resolution ($\Delta E/E$) of 2×10^{-4} . The XAS spectra were averaged for four scans. The resulting data were baseline-corrected and edge-normalized using ARTENA software.^[36]

Oxidation of Cyclohexene: Cyclohexene (2.4 mmol), TBHP or isobutyraldehyde, the MIL-53[Cu] catalyst, and *n*-nonane (0.24 mmol, internal standard) were added into a stainless-steel reactor containing solvent (24 mL). The reactor was purged with an appropriate gas for five cycles and then pressurized to the desired pressure. The reaction mixture was stirred and heated at 50 °C. After a certain time, the reaction was quickly cooled to room temperature, the catalyst was filtered out, and the substrate conversion and the product selectivity were determined by GCMS (Agilent 7890A with 5975 MSD), equipped with an HP-5 capillary column (polydimethylsiloxane with 5 % phenyl group, 20 m length, 0.25 mm i.d., 0.25 μm film thickness).

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Keywords: Metal–organic frameworks · Olefins · Postsynthetic modification · Oxidation · Copper

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