



REGULAR ARTICLE

One-pot synthesis of bimetal MOFs as highly efficient catalysts for selective oxidation of styrene

KAI HUANG* , SIBING YU, XIAOXIN LI  and ZHENYU CAI

School of Chemistry and Chemical Engineering, Southeast University, Jiangning District, Nanjing 211189, China

E-mail: huangk@seu.edu.cn

Kai Huang and Sibing Yu have contributed equally to this work.

MS received 4 June 2020; revised 21 July 2020; accepted 10 August 2020

Abstract. A series of novel bimetallic organic framework materials ($\text{Cu}_x\text{-Co}_y\text{-MOF}$) have been successfully prepared by a simple one-pot synthetic method, and their characters were evaluated *via* means of various techniques. The tested data showed a series of $\text{Cu}_x\text{-Co}_y\text{-MOFs}$ displayed good crystallinity and the doping of Co in original Cu-based framework would not change the morphology of the MOF catalysts. The catalytic activity of prepared materials was tested in the catalytic oxidation of styrene in the presence of TBHP. The effects of reaction time, reaction temperature and other reaction conditions on catalytic performance were systematically studied. The results revealed that the introduction of Co can improve the selectivity to form epoxides and reduce the yield of benzaldehyde without affecting the conversion rate of catalytic oxidation reaction of styrene. Excitingly, the $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ showed better catalytic performance than Cu-MOF and Co-MOF under the optimal reaction conditions, the conversion rate of styrene reached 97.81%, and styrene oxide selectivity reached 83.04%, which indicated a significant synergistic effect of the Cu/Co bimetallic MOF. Furthermore, the $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst exhibited good reusability that could be reused at least four times without significant inactivation.

Keywords. Bimetallic MOF; styrene; oxidation reaction; synergistic effect.

1. Introduction

The catalytic oxidation of styrene is an important reaction that has been paid close attention to by many researchers because styrene oxide as an organic intermediate was widely used in the synthesis of cosmetics, perfume and medicine.^{1,2} Numerous researchers over the past few decades have been working on catalysts that catalyze the oxidation of styrene. At present, homogeneous catalysts including transition metal-Schiff base coordination compounds and heteropoly acids have been widely used in olefin catalytic oxidation systems.³⁻⁵ Although homogeneous catalysts have a high activity in catalytic oxidation of styrene, they are difficult to separate from the reaction system and cannot be effectively recycled.⁶ In contrast, the

heterogeneous catalysts formed by fixing homogeneous catalysts on various carriers including zeolites, organic polymers, Al_2O_3 and so on, which perfectly avoid the defects of homogeneous catalysts. Whereupon, many multiphase catalysts for the oxidation of olefin have been reported based on this advantage.⁷⁻¹² Although homogeneous catalysts can be used to catalyze reactions by immobilizing solid supported catalysts, problems such as more complex preparation methods, heterogeneous catalytic activity centers, and poor thermal stability still need to be further improved and addressed by researchers. Therefore, it is still a very significant work to further explore the multiphase catalysts for the oxidation of styrene.

Metal-organic framework (MOF) is a new kind of porous materials composed of metal nodes and

*For correspondence

organic connectors. MOF has become one of the most interesting catalytic materials due to its high specific surface area, adjustable channel size and easy functionalization of ligands, which are conducive to the diffusion of reactants and products in the catalytic process.^{13–17} In addition, the wide distribution of metal components in MOFs can also serve as active sites for catalytic reactions, making them promising candidates for catalytic oxidation of styrene. In general, the efficiency of MOF catalyzing the oxidation of styrene is closely related to its metal components. With the development of the research on the oxidation of styrene, it is found that the epoxidation of styrene mainly tends to the development and application of polyphase transition metal catalysts, among which the catalysts with copper, cobalt and nickel as the main active species have attracted much attention because of their high conversion rate of styrene.^{18–21} Considering the possible synergistic effect of the two active metals in the catalytic process, the introduction of additional active metal centers in the original MOFs is an effective way to improve its catalytic performance, which has also attracted extensive attention in recent years.^{22,23} For example, the Mircea Dinca team prepared Mn-MOF-5 by replacing part of the Zn^{II} in MOF-5 with Mn^{II} and using it as a catalyst to catalyze the oxidation of cyclohexene to epoxide cyclohexane under oxygen conditions, with a selectivity of up to 99%.²⁴ In addition, in the early stage, our team also introduced Cu/Ni into NH₂-MIL-101 (Cr) through the post-synthesis modification method to synthesize a series of Cu/Ni salen@NH₂-MIL-101 (Cr) for catalytic oxidation of styrene, in which the conversion rate of styrene was as high as 98.78%, and that of styrene oxide was as high as 89.58%.²⁵ However, the preparation process of the bimetallic MOF material synthesized by the post-modification method is relatively complicated. On the contrary, the direct co-doping method and the hydrothermal reaction by the one-pot method to generate the bimetallic catalyst makes the preparation process simpler.

Here, Cu_x-Co_y-MOF were synthesized by using hydrothermal reaction co-doping Co to Cu-MOF in one-pot method and used as a catalyst for styrene oxidation, which simplifies the preparation process of bimetal MOFs compared with the traditional post-modification method. In addition, the test data showed that the catalytic oxidation performance of styrene was significantly improved after Co was doped into Cu-MOF, among which the most exciting was that the selectivity of the target product styrene oxide was greatly improved.

2. Experimental

2.1 Materials and methods

Copper(II) nitrate trihydrate [Cu(NO₃)₂·3H₂O], cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O], acetonitrile (CH₃CN), anhydrous ethanol (EtOH) and N,N-Dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co. Shanghai, China. Tert-Butyl hydroperoxide (TBHP), trimesic acid (H₃BTC) and styrene were purchased from Aladdin Chemistry Co. Shanghai, China. And all reagents were used without extra purification.

2.2 Synthesis methods

2.2a Synthesis Cu-MOF: The Cu-MOF crystal was prepared using a slightly modified procedure in the literature.²⁶ Briefly, a mixture of Cu(NO₃)₂·3H₂O and H₃BTC was dissolved in combination of a 1:1(v/v) DMF and EtOH solution, and stirred magnetically for 20 min. The above mixtures were put in a Teflon autoclave and maintained at 110 °C for 60 h. After that, the autoclave was cooled naturally to the ambient temperature, and the solid product was washed with a water–ethanol mixture to remove unreacted H₃BTC. Finally, the purified Cu-MOF was collected after filtration and dried overnight under vacuum at 110 °C.

2.2b Synthesis Cu_x-Co_y-MOF: The preparation method of Cu_x-Co_y-MOF catalytic material is the same as the synthesis method of Cu-MOF while using Co(NO₃)₂·6H₂O instead of Cu(NO₃)₂·3H₂O by the starting Co/Cu molar ratios of 1:3, 1:1, and 3:1, respectively. Similarly, if the x in Cu_x-Co_y-MOF is zero, it is only necessary to replace all Cu(NO₃)₂·3H₂O with Co(NO₃)₂·6H₂O to obtain Co-MOF through the same synthesis process and conditions.

2.3 Catalyst characterization

Powder X-ray diffraction (PXRD) patterns of the prepared catalysts were obtained in the range of 5–50° to identify the structures on an Ultima IV X-ray diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) operating at 200 mA and 40 kV.

Fourier transform infrared (FT-IR) spectra of the catalysts were recorded on a Thermo Fisher Nicolet 5700 spectrophotometer in the range of 500–4000 cm⁻¹.

Scanning electron microscopy images of the catalysts were observed using a scanning electron microscope (SEM, TESCAN 5136 MM) operating at 15 kV. The metal contents in the catalysts were determined by inductive coupled plasma optical emission spectrometer (ICP-OES) using Varian Varian 720-ES. The compositions and chemical states of surface elements the prepared catalysts were detected by X-ray photoelectron spectroscopy (XPS) which was carried out on Thermo Fisher ESCALAB 250Xi system equipped with a monochromatic Al K α (1486.6 eV) irradiation. For all MOF catalysts tested, the binding energies (B.E.) value of the C 1s peak at 284.6 eV was used as an internal reference to calibrate each atom spectrum.

2.4 Catalytic performance test

The catalytic oxidation of styrene reaction was performed in a 50 mL three-necked flask equipped with a condenser. Typically, 60 mg of catalyst, 10 mmol of styrene and 10 mL of acetonitrile were added to 50 mL three-necked flask sequentially, after which the flask was immersed in a thermostatic oil bath with magnetic stirring. Subsequently, 70% TBHP was added quickly to the reactor as the reaction temperature approached. After the reaction, the reaction system was cooled slowly down to the ambient temperature. The product was centrifuged from the catalyst and detected by gas chromatograph (INESA GC-126) equipped with a flame ionization detector and a chromatographic column (Figure S1 in Supplementary Information).

3. Results and Discussion

3.1 Catalyst characterization

The crystallinity of various synthesized MOF catalysts was studied by Powder X-ray diffraction (PXRD) patterns. As shown in Figure 1, the synthesized Cu-MOF PXRD patterns are in good agreement with the theoretical simulation patterns of Cu-MOF²⁷, indicating that Cu-MOF has been successfully synthesized. In addition, the PXRD patterns of the synthesized Cu_{0.75}-Co_{0.25}-MOF, Cu_{0.5}-Co_{0.5}-MOF and Cu_{0.25}-Co_{0.75}-MOF were compared with the PXRD patterns of Cu-MOF. The results showed that the characteristic peaks of Cu_x-Co_y-MOF synthesized with Co were very similar to Cu-MOF, which was consistent with the results previously reported.^{28,29} At the same time, it can be seen from the PXRD pattern of the prepared compounds that the crystallinity of Cu_x-Co_y-MOF is

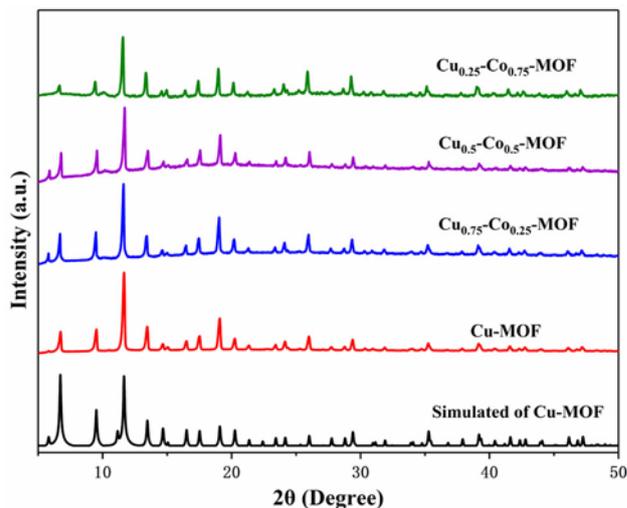


Figure 1. The PXRD patterns of Cu-MOF and its simulation, Cu_{0.75}-Co_{0.25}-MOF, Cu_{0.5}-Co_{0.5}-MOF and Cu_{0.25}-Co_{0.75}-MOF.

relatively high, which also indicates that the generated co-doped MOF still retains the structure.

FT-IR spectrums of Cu-MOF and Cu_x-Co_y-MOF were exhibited in Figure 2. By comparing the infrared spectra of H₃BTC (Figure S2, Supplementary Information), the corresponding infrared absorption peaks observed can be used to predict the main functional groups of the structure. The absorption peak in the 1628-1370 cm⁻¹ region is caused by the symmetric and asymmetric vibration of the organic ligand BTC³⁻.³⁰ Among them, the characteristic peak around 1628-1565 cm⁻¹ is caused by the asymmetric stretching vibration of the carboxyl group, while the characteristic peak in 1445-1370 cm⁻¹ is caused by

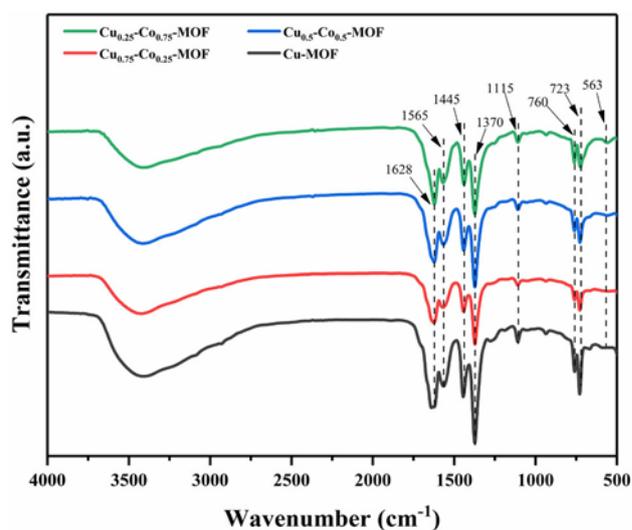


Figure 2. The FT-IR spectrums of Cu-MOF, Cu_{0.75}-Co_{0.25}-MOF, Cu_{0.5}-Co_{0.5}-MOF and Cu_{0.25}-Co_{0.75}-MOF.

the symmetric stretching vibration of the carboxyl group. In addition, there was no significant characteristic peak in the region of $1726\text{--}1680\text{ cm}^{-1}$, indicating the deprotonation of trimesic acid, indicating that carboxylate ions were involved in the formation of the complex. At the same time, the vibration of hydroxide ($\sim 3600\text{ cm}^{-1}$) has no obvious absorption band, indicating that the ethanol molecule is not bound to the synthesized MOF material.^{31,32} All these indicate that metal salts have reacted with the organic ligands and coordinated successfully.

To observe the surface morphology of MOF catalytic materials, Cu-MOF, $\text{Cu}_{0.75}\text{-Co}_{0.25}\text{-MOF}$, $\text{Cu}_{0.5}\text{-Co}_{0.5}\text{-MOF}$ and $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ were scanned by SEM after gold spraying. It can be seen from the SEM image (Figure 3a) that the crystal sample of Cu-MOF has a well-defined octahedral shape. Besides, as observed from Figure 3b, Figure 3c and Figure 3d, the SEM images of $\text{Cu}_x\text{-Co}_y\text{-MOF}$ reserved a regular octahedral structure with about $5\text{--}20\text{ }\mu\text{m}$ width like Cu-MOF, which indicates that Co doping does not change the morphology of the crystal structure.³³ Such a regular structure indicated the excellent crystallization of the material which was already proved by its power X-ray diffraction pattern of the catalysts.

The contents of Cu and Co, and the real molar ratio of Cu/Co in all the synthesized bimetal $\text{Cu}_x\text{-Co}_y\text{-MOF}$ were determined by ICP-OES, as shown in Table 1. These measurement results perfectly validate the existence of copper and cobalt metal elements in the synthesized $\text{Cu}_x\text{-Co}_y\text{-MOF}$ materials, and the actual molar ratio of Cu/Co metal in each bimetal MOF is basically consistent with the experimental value, which also indicating Cu and Co bimetallic MOFs were successfully prepared.

The surface compositions and chemical states of the prepared catalysts (Cu-MOF and $\text{Cu}_x\text{-Co}_y\text{-MOF}$) were studied by XPS. The XPS survey spectrum (Figure S3, Supplementary Information) of the five MOF materials illustrated the peaks of three common elements present in the catalysts (i.e., C, N, and O). Besides, Cu exists in Cu-MOF and $\text{Cu}_x\text{-Co}_y\text{-MOF}$, while Co is detected in both Co-MOF and $\text{Cu}_x\text{-Co}_y\text{-MOF}$, which further demonstrating the successful fabrication of Cu-MOF, Co-MOF and $\text{Cu}_x\text{-Co}_y\text{-MOF}$ catalytic materials.

The C 1s spectrum of five MOFs in Figure S4 (Supplementary Information) can be reasonably fitted with five symmetrical peaks centered at 284.6, 285.9, 286.6, 288.3 and 289.8 eV, which correspond to the bonds of C-C, C-N, C-O, C=O and O-C=O,

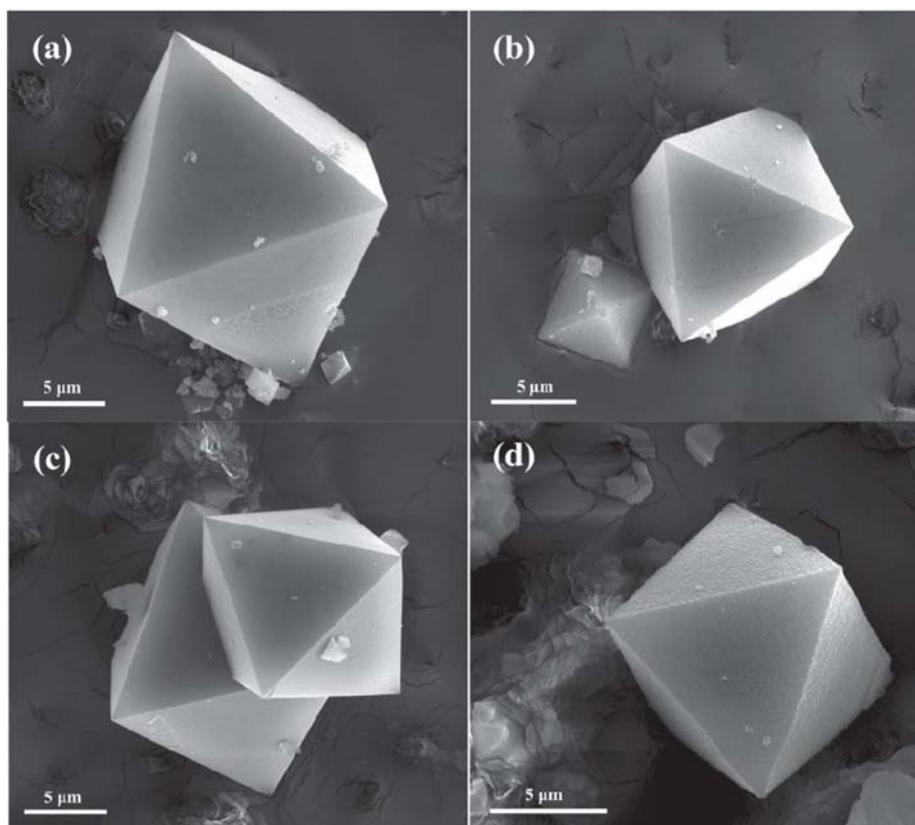


Figure 3. The SEM images of (a) Cu-MOF, (b) $\text{Cu}_{0.75}\text{-Co}_{0.25}\text{-MOF}$, (c) $\text{Cu}_{0.5}\text{-Co}_{0.5}\text{-MOF}$ and (d) $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$.

Table 1. The concentrations of Cu and Co inside the synthesized bimetal MOF samples, as determined by ICP-OES.

Sample	Weight (g)	Detected element	Content (mg/kg)	Molar ratio (Cu/Co)
Cu _{0.75} -Co _{0.25} -MOF	0.0383	Cu	174410.6	3.29
	0.0383	Co	49129.5	
Cu _{0.5} -Co _{0.5} -MOF	0.272	Cu	11922.7	1.08
	0.272	Co	10246.0	
Cu _{0.25} -Co _{0.75} -MOF	0.356	Cu	7160.9	0.40
	0.356	Co	16425.0	

respectively.^{34,35} Moreover, DMF was used as a solvent during the MOF synthesis and it was not completely removed by filtration/washing from the MOF materials, the existence of the C-N bond and N 1s confirms this.

Figure 4(a) is a spectral image of Co 2p XPS which is fitted by using symmetric components and related satellite lines. From the image, Co 2p decomposes to form the 2p_{3/2} and 2p_{1/2} peaks, accompanied by the 2p_{3/2} satellite peaks and 2p_{1/2} satellite peaks. These spin-orbit peaks and vibration satellite peaks indicate that Co exists as Co(II) in Co-MOF and Cu_x-Co_y-MOF.³⁶

As can be seen from Figure 4(b), the 2p_{3/2} and 2p_{1/2} peaks formed by the spin-splitting of Cu element Cu 2p electron in the copper-containing catalyst are also accompanied by the shake-up satellite peak. According to the XPS results of Cu 2p, the main characteristic peak of Cu 2p_{3/2} at 933.2 eV and 935 eV and the two peaks of 2p_{1/2} can be fitted with at 953 eV and 955 eV

indicate the presence of Cu²⁺ in the catalyst. Besides, two vibration satellite peaks were observed in the range of 937 eV-948 eV, which further indicated that copper species mainly existed on the surface of Cu-MOF and Cu_x-Co_y-MOF samples in the form of Cu(II). At the same time, it is not difficult to discover that compared with Cu-MOF, the peak relative strength of Cu_x-Co_y-MOF samples at 933.2 eV is significantly reduced, which may be caused by the change in electron density around Cu(II) caused by the Co species doped in the sample.^{37,38}

3.2 Catalytic oxidation of styrene

The catalytic activities of Cu-MOF, Co-MOF, Cu_x-Co_y-MOF and H₃BTC, homogeneous copper salt and homogeneous cobalt salt were measured for the oxidation of styrene in the presence of oxidant and solvent as shown in Table 2 (all data in Table 2 are the

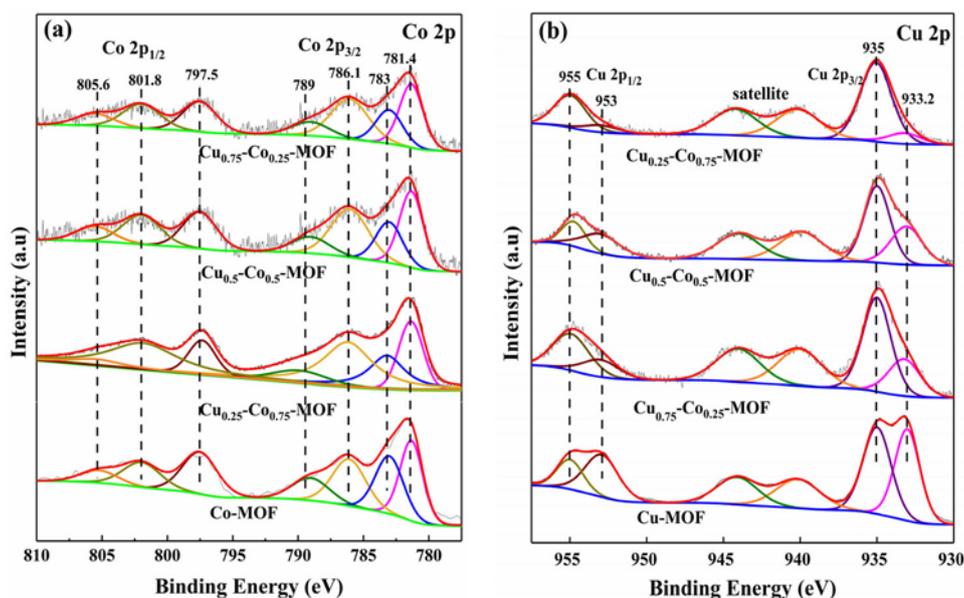


Figure 4. (a) The Co 2p XPS spectra of the Co-MOF and Cu_x-Co_y-MOF; (b) the Cu 2p XPS spectra of the Cu-MOF and Cu_x-Co_y-MOF.

Table 2. Catalytic activities and selectivities of various catalysts for the oxidation of styrene.

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			A	B	C
1	None	–	–	–	–
2	H ₃ BTC	–	–	–	–
3	Cu(NO) ₂ ·3H ₂ O	52.25	7.43	88.85	3.72
4	Co(NO) ₂ ·6H ₂ O	40.32	21.64	74.11	4.25
5	Co-MOF	72.42	77.72	21.45	0.83
6	Cu-MOF	92.46	33.91	60.21	5.88
7	Cu _{0.75} -Co _{0.25} -MOF	97.86	51.07	45.19	3.74
8	Cu _{0.5} -Co _{0.5} -MOF	97.92	69.25	27.62	3.13
9	Cu _{0.25} -Co _{0.75} -MOF	97.81	83.04	14.04	2.92

Reaction conditions: 60 mg of catalysts, 10 mmol of styrene, 10 mL of acetonitrile, 30 mmol of TBHP, 80 °C, 8 h.

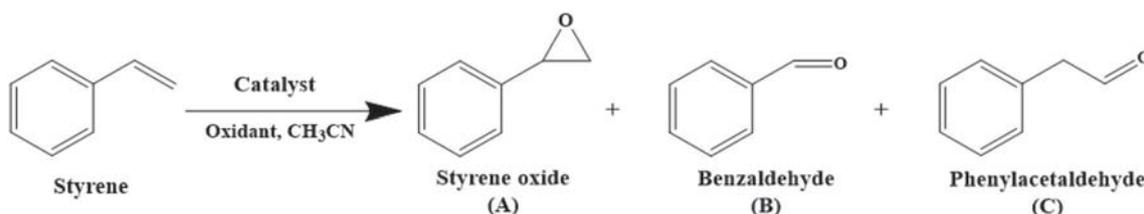
average value of three sets of catalysis experimental results, and the detailed supplementary data can be seen in Table S1, Supplementary Information). The schematic diagram of styrene catalytic oxidation reaction is shown in Scheme 1.

Compared with the MOF catalytic materials produced by the reaction of M²⁺ and H₃BTC, blank reaction was carried out using only TBHP and acetonitrile, and the results of this experiment showed that the styrene oxidation will not occur in the absence of any catalyst. (Table 2, Entry 1). Then, to identify the catalytic sites on the MOF for styrene oxidation, the reaction was in the presence of H₃BTC and without other catalysts. Similarly, the reaction products were still not detected when H₃BTC was used as a catalyst, indicating that the constituent metal nodes (M²⁺ in the MOFs structure) were the catalytic active sites (Table 2, Entry 2). In addition, it can be seen from the experimental results of Entry 3-4 in Table 2, that the homogeneous copper salt and homogeneous cobalt salt had certain catalytic effect on styrene oxidation reaction. Again, the results of styrene oxidation reaction catalyzed by homogeneous metal salts further support that the metal nodes in MOF structure were the catalytic activity for styrene oxidation reaction. Unfortunately, the selectivity of target products were

relatively low and homogeneous metal salts could not be recovered.

According to the experimental results of MOF catalysts, Cu-MOF catalyst has a good catalytic activity, which enables the conversion of most styrene to produce styrene oxide (A) and benzaldehyde (B), and the reaction will generate a small amount of phenylacetaldehyde (C), which may be due to the further oxidation of some epoxides in the presence of TBHP. However, it is a pity that Cu-MOF catalyzed oxidation of styrene produces mainly benzaldehyde, and only a relatively small amount of target product ethylene oxide. An interesting result from Co-MOF catalyzed styrene was found to be relatively low in catalytic activity, but it had a better selectivity for conversion of styrene to styrene oxide (A).

It is noteworthy that Cu/Co bimetallic MOF catalytic material not only has high catalytic activity in the oxidation of styrene but also can selectively catalyze the synthesis of styrene oxide as the target product. According to the experimental data in Table 2 (Entry 5-9), the catalyst doped with Co²⁺ in Cu-MOF can promote the selective conversion of styrene to styrene oxide and reduce the yield of benzaldehyde. In addition, it can be concluded from the experimental data that the selective conversion of

**Scheme 1.** Oxidation of styrene using catalyst.

styrene oxide can be improved continuously by gradually increasing the content of Co^{2+} in $\text{Cu}_x\text{-Co}_y\text{-MOF}$ materials, and the conversion rate of styrene is hardly affected. To be specific, the selectivity of product A increased from 51.07% ($\text{Cu}_{0.75}\text{-Co}_{0.25}\text{-MOF}$) to 83.04% ($\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$), which also significantly reduced the selectivity of benzaldehyde B from 45.19% to 14.04%. Furthermore, these catalysts were able to maintain the conversion rate of styrene at least 97.81%.

All the above experimental results indicated a significant synergistic effect of the Cu/Co bimetallic MOF as compared to Cu-MOF and Co-MOF, and such synergistic effect has also been observed in many bimetallic catalysts.^{39,40}

3.3 Optimization of the reaction conditions

The effects of reaction temperature and reaction time on the reaction products were investigated by using $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ as a catalyst for the oxidation of styrene. TBHP (70% weight % aqueous solution) was used as the oxidant to catalyze the reaction (8 h). The effect of reaction temperature on the selective oxidation of styrene was shown in Figure 5. It is clearly observed that the conversion rate of styrene increases with the increase of reaction temperature, and the selectivity of ethylene oxide also increases gradually. When the reaction temperature is 60 °C, the conversion rate of styrene is 70.20% along with a 49.62% selectivity of styrene oxide. When the temperature was further raised to 80 °C, the conversion rate of styrene and the selectivity of styrene oxide increased to

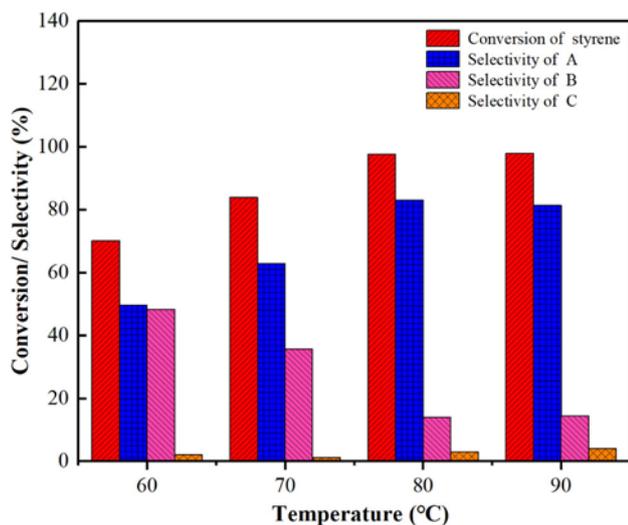


Figure 5. Effects of reaction temperature on the activity: styrene 10 mmol, acetonitrile 10 mL, TBHP 30 mmol, reaction time 8 h, 60 mg of $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst.

97.81% and 83.04%, respectively, indicating that high temperature can promote the catalytic oxidation of styrene. However, as the reaction temperature increased to 90 °C, the selectivity of the target product was decreased, while that of phenylacetaldehyde was increased, which may be because further catalytic oxidation of styrene oxide to phenylacetaldehyde is more likely to occur at 90 °C. Therefore, the optimum reaction temperature of $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst for styrene oxidation is 80 °C.

Then, the reaction temperature was controlled at 80 °C to study the effect of reaction time on the catalytic oxidation of styrene, as shown in Figure 6. With increasing reaction time, the conversion rate of styrene

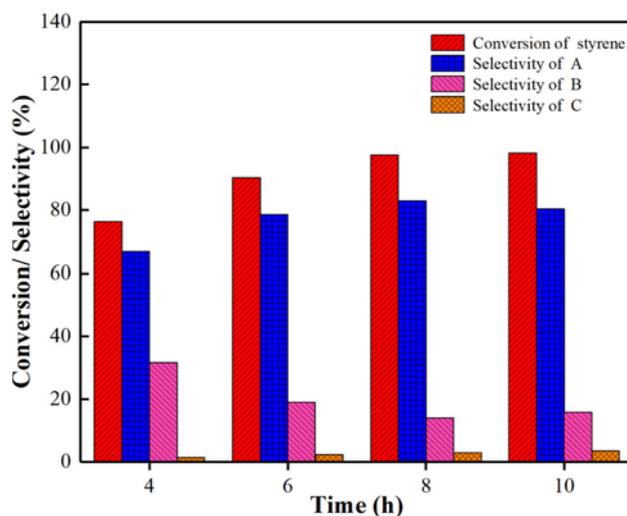


Figure 6. Effects of reaction time: styrene 10 mmol, acetonitrile 10 mL, TBHP 30 mmol, reaction temperature 80 °C, 60 mg of $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst.

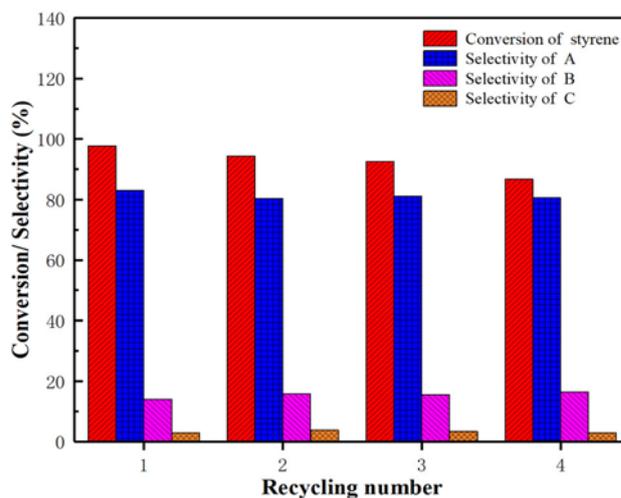


Figure 7. The recyclability of the $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ sample. Reaction conditions: styrene 10 mmol, acetonitrile 10 mL, TBHP 30 mmol, reaction time 8 h, reaction temperature 80 °C, 60 mg of $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst.

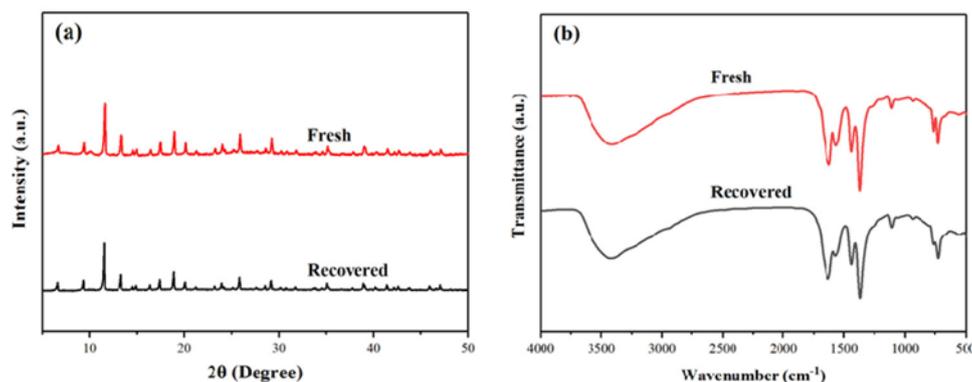


Figure 8. (a) The PXRD patterns of the fresh and recovered $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst and (b) the FT-IR spectra of the fresh and recovered $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst.

significantly increases, and the selectivity of styrene oxide was also improved. However, the yield of styrene oxide did not increase significantly after the reaction time increased to 8 h. Thus, the reaction time of 8 h was promising to be the optimum reaction time.

3.4 Recycling performance of the catalyst

It is well known that the recyclability of catalysts is one of the key indexes for evaluating catalytic materials. The recoverability of $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst in selective catalytic oxidation of styrene was tested. The catalyst is easily separated from the reaction mixture by centrifugation, washed with ethanol three times and then dried for recycling. As shown in Figure 7, $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst exhibited good catalytic stability in the four cycles, and the conversion rate of styrene decreased slightly while the selectivity of styrene oxide remained unchanged, indicating that the catalytic activity was not affected and high recyclability for the $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst. Additionally, the used catalyst after using four times was studied *via* Powder X-ray diffraction and Fourier transform infrared and compared with the fresh $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst before use. It is not difficult to observe from Figure 8 that the PXRD pattern and FT-IR spectra of the recovered $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst are practically identical to the fresh catalysts, which further confirms the structure stability of the catalyst developed in this study.

4. Conclusions

In this paper, copper and cobalt bimetallic MOF material ($\text{Cu}_x\text{-Co}_y\text{-MOF}$) as a neoteric catalyst for the oxidation of styrene was prepared using a simple solvothermal method. The results showed that the

$\text{Cu}_x\text{-Co}_y\text{-MOF}$ has significantly improved the selective oxidation of styrene to styrene oxide with Tert-butanol hydrogen peroxide as efficient oxidant compares to Cu-MOF , which imply the introduction of Co into Cu-MOF to synthesize bimetallic MOF catalyst is more effective for styrene selective oxidation. In other words, Co^{2+} can increase the yield of styrene oxide and reduce the generation of by-products. According to the experimental data, the selectivity of styrene oxide can achieve 83.04% with 97.81% styrene conversion and the 81.22% styrene oxide yield by using $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ as catalyst under the optimum reaction condition. In addition, the $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ catalyst synthesized in this paper exhibits satisfactory recyclability. The synergic effects of bimetallic organic porous material are also observed on the catalytic oxidation for styrene, demonstrating the possibility of introducing all sorts of metal ions to MOFs by one-pot synthesis, to improve their catalytic properties for various chemical reactions.

Acknowledgement

This study was funded by the National Natural Science Foundation of China (No. 21576049) and the Fundamental Research Funds for the Central Universities (No. 2242016K40082).

Supplementary Information (SI)

Figures S1-S4 and Table S1 are available at www.ias.ac.in/chemsci.

References

1. Dhakshinamoorthy A, Alvaro M and Garcia H 2011 Aerobic Oxidation of Styrenes Catalyzed by an Iron Metal Organic Framework *ACS Catal.* **1** 836

- Hammer S C, Kubik G, Watkins E, Huang S, Mingos D M P and Arnold F H 2017 Anti-Markovnikov alkene oxidation by metal-oxo-mediated enzyme catalysis *Science* **358** 215
- Cozzi P G 2004 Metal–Salen Schiff base complexes in catalysis: practical aspects *Chem. Soc. Rev.* **33** 410
- Gupta K C and Sutar A K 2008 Catalytic activities of Schiff base transition metal complexes *Coord. Chem. Rev.* **252** 1420
- Yamada T, Sakakura A, Sakaguchi S, Obora Y and Ishii Y 2008 Oxidative arylation of ethylene with benzene catalyzed by Pd(OAc)₂/heteropoly acid/O₂ system *New J. Chem.* **32** 738
- Shylesh S, Schnemann V and Thiel W R 2010 Magnetically Separable Nanocatalysts: Bridges between Homogeneous and Heterogeneous Catalysis *Angew. Chem. Int. Ed.* **49** 3428
- Yang Y, Zhang Y, Hao S J and Kan Q B 2011 Tethering of Cu(II), Co(II) and Fe(III) tetrahydro-salen and salen complexes onto amino-functionalized SBA-15: Effects of salen ligand hydrogenation on catalytic performances for aerobic epoxidation of styrene *Chem. Eng. J.* **171** 1356
- Gupta K C, Sutar A K and Lin C C 2009 Polymer-supported Schiff base complexes in oxidation reactions *Coord. Chem. Rev.* **253** 1926
- Hossain M M, Atanda L, Al-Yassir N and Al-Khattaf S 2012 Kinetics modeling of ethylbenzene dehydrogenation to styrene over a mesoporous alumina supported iron catalyst *Chem. Eng. J.* **207–208** 308
- Pan D H, Xu Q, Dong Z Y, Chen S W, Yu F, Yan X L, Fan B B and Li R F 2015 Facile synthesis of highly ordered mesoporous cobalt–alumina catalysts and their application in liquid phase selective oxidation of styrene *RSC Adv.* **5** 98377
- Wang X F, Wu S J, Li Z F, Yang X Y, Su H J, Hu J, Huo Q S, Guan J Q and Kan Q B 2016 Cu(II), Co(II), Fe(III) or VO(II) Schiff base complexes immobilized onto CMK-3 for styrene epoxidation *Micropor. Mesopor. Mater.* **221** 48
- Thao N T and Huyen L T K 2015 Catalytic oxidation of styrene over Cu-doped hydrotalcites *Chem. Eng. J.* **279** 840
- Jiao L, Wang Y, Jiang H L and Xu Q 2018 Metal–Organic Frameworks as Platforms for Catalytic Applications *Adv. Mater.* **30** 1703663
- Furukawa H, Cordova K E, O’Keeffe M and Yaghi O M 2013 The Chemistry and Applications of Metal–Organic Frameworks *Science* **341** 1230444
- Lee J Y, Farha O K, Roberts J, Scheidt K A, Nguyen S T and Hupp J T 2009 Metal–organic framework materials as catalysts *Chem. Soc. Rev.* **38** 1450
- Yang Q H, Xu Q and Jiang H L 2017 Metal–organic frameworks meet metal nanoparticles: synergistic effect for enhanced catalysis *Chem. Soc. Rev.* **46** 4774
- Wu C D, Hu A G, Zhang L and Lin W B 2005 A Homochiral Porous Metal–Organic Framework for Highly Enantioselective Heterogeneous Asymmetric Catalysis *J. Am. Chem. Soc.* **127** 8940
- Huang K, Guo L L and Wu D F 2015 Synthesis of nanorod MOF catalyst containing Cu²⁺ and its selective oxidation of styrene *Mater. Res. Express.* **6** 125101
- Wu Y, Wang W, Liu L L, Zhu S N, Wang X C, Hu E Z and Hu K H 2019 Novel Synthesis of Cu–Schiff Base Complex@Metal–Organic Framework MIL-101 via a Mild Method: A Comparative Study for Rapid Catalytic Effects *ChemistryOpen* **8** 33
- Ramanathan R and Sugunan S 2007 Styrene oxidation by H₂O₂ using Ni–Gd ferrites prepared by co-precipitation method *Catal. Commun.* **8** 1521
- Huang K, Wang Z L and Wu D F 2018 Synthesis of well-ordered MCM-41 containing highly-dispersed NiO nanoparticles and efficient catalytic epoxidation of styrene *J. Chem. Sci.* **130** 62
- Huang Y B, Liang J, Wang X S and Cao R 2017 Multifunctional metal–organic framework catalysts: synergistic catalysis and tandem reactions *Chem. Soc. Rev.* **46** 126
- Liu H L, Fang R Q, Li Z and Li Y W 2015 Solventless hydrogenation of benzene to cyclohexane over a heterogeneous Ru–Pt bimetallic catalyst *Chem. Eng. J.* **122** 350
- Stubbs A W, Braglia L, Borfecchia E, Meyer R J, Roman-Leshkov Y, Lamberti C and Dinca M 2018 Selective Catalytic Olefin Epoxidation with Mn^{II}-Exchanged MOF-5 *ACS Catal.* **8** 596
- Huang K, Guo L L and Wu D F 2019 Synthesis of Metal Salen@MOFs and Their Catalytic Performance for Styrene Oxidation *Ind. Eng. Chem. Res.* **58** 4744
- Lin S, Song Z L, Che G B, Ren A, Li P, Liu C B and Zhang J H 2014 Adsorption behavior of metal-organic frameworks for methylene blue from aqueous solution *Micropor. Mesopor. Mater.* **193** 27
- Wu Y, Kobayashi A, Halder G J, Peterson V K, Chapman K W, Lock N, Southon P D and Kepert C J 2008 Negative Thermal Expansion in the Metal–Organic Framework Material Cu₃(1,3,5-benzenetricarboxylate)₂ *Angew. Chem. Int. Ed.* **47** 8929
- Zhao G H, Liu Q, Tian N, Yu L and Dai W 2018 Highly Efficient Benzothiophene Capture with a Metal-Modified Copper-1,3,5-Benzenetricarboxylic Acid Adsorbent *Energy Fuels* **32** 6763
- Qin Y H, Huang L, Zhang L and He H B 2019 One-step synthesis of confined ion Ag_x-Cu-BTC for selective catalytic reduction of NO with CO *Inorg. Chem. Commun.* **102** 130
- Maiti S, Pramanik A, Manju U and Mahanty S 2015 Reversible Lithium Storage in Manganese 1,3,5-Benzenetricarboxylate Metal–Organic Framework with High Capacity and Rate Performance *ACS Appl. Mater. Interfaces* **7** 16357
- Feng C, Guo C Y, Hu D, Guo J, Cao X L, Akram N and Wang J D 2018 Catalytic performance of Co 1,3,5-benzenetricarboxylate in the conversion of CO₂ to cyclic carbonates *React. Kinet. Mech. Cat.* **125** 633
- Li C, Lou X B, Shen M, Hu X S, Guo Z, Wang Y, Hu B W and Chen Q 2016 High Anodic Performance of Co 1,3,5-Benzenetricarboxylate Coordination Polymers for Li-Ion Battery *ACS Appl. Mater. Interfaces* **8** 15352
- Wang T T, Li X X, Dai W, Fang Y Y and Huang H 2015 Enhanced adsorption of dibenzothiophene with zinc/copper-based metal–organic frameworks *J. Mater. Chem. A* **3** 21044

34. Wang P C, Zhou Y K, Hu M and Chen J 2017 Well-dispersed NiO nanoparticles supported on nitrogen-doped carbon nanotube for methanol electrocatalytic oxidation in alkaline media *Appl. Surf. Sci.* **392** 562
35. Tu X F, Zhou Y K and Song Y J 2017 Freeze-drying synthesis of three-dimensional porous LiFePO₄ modified with well-dispersed nitrogen-doped carbon nanotubes for high-performance lithium-ion batteries *Appl. Surf. Sci.* **400** 329
36. Wu Y F, Song X H, Xu S Q, Zhang J H, Zhu Y L, Gao L J and Xiao G M 2019 2-Methylimidazole Modified Co-BTC MOF as an Efficient Catalyst for Chemical Fixation of Carbon Dioxide *Catal. Lett.* **149** 2575
37. Tang J T and Wang J L 2020 Iron-copper bimetallic metal-organic frameworks for efficient Fentonlike degradation of sulfamethoxazole under mild conditions *Chemosphere* **241** 125002
38. Huang Q Q, Chen Y, Yu H Q, Yan L G, Zhang J H, Wang B, Du B and Xing L T 2018 Magnetic graphene oxide/MgAl-layered double hydroxide nanocomposite: One-pot solvothermal synthesis, adsorption performance and mechanisms for Pb²⁺, Cd²⁺, and Cu²⁺ *Chem. Eng. J.* **341** 1
39. Feng C, Wang Y N, Gao S T, Shang N Z and Wang C 2016 Hydrogen generation at ambient conditions: AgPd bimetal supported on metal-organic framework derived porous carbon as an efficient synergistic catalyst *Catal. Commun.* **78** 17
40. Orcajo G, Villajos J A, Martos C, Botas J A and Calleja G 2015 Influence of chemical composition of the open bimetallic sites of MOF-74 on H₂ adsorption *Adsorption* **21** 589