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Article

Solvothermal synthesis of Co-substituted phosphomolybdate acid encapsulated in the UiO-66 framework for catalytic application in olefin epoxidation

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ABSTRACT

Hybrid composites of phosphomolybdic acid@UiO-66 ($\text{PMo}_{12}\text{@UiO-66}$) and Co-substituted phosphomolybdic acid@UiO-66 ($\text{PMo}_{11}\text{Co@UiO-66}$) were synthesized using the direct solvothermal method. A variety of characterization results demonstrated that phosphomolybdic acid (PMo_{12}) or Co-substituted phosphomolybdate acid (PMo_{11}Co) clusters are uniformly dispersed in the cages of Zr-based metal-organic UiO-66 frameworks. The catalytic properties of these hybrid composites were investigated by applying the epoxidation of olefins with *tert*-butyl hydroperoxide as the oxidant. Compared to $\text{PMo}_{12}\text{@UiO-66}$, $\text{PMo}_{11}\text{Co@UiO-66}$ showed a much higher catalytic activity and was simply recovered by filtration and reused for at least ten runs without significant loss of catalytic activity. Particularly, $\text{PMo}_{11}\text{Co@UiO-66}$ can efficiently convert cyclic olefins like limonenes to epoxides, and its selectivity to 1,2-limonene oxide reached 91% in the presence of a radical inhibitor such as hydroquinone. The excellent catalytic activity and stability of the hybrid composite $\text{PMo}_{11}\text{Co@UiO-66}$ are mainly attributed to the uniform distribution of highly active PMo_{11}Co units within the smaller cages of UiO-66, to the suitable surface polarity of the hybrid composite for facilitating the access of reagents and solvent, and to the strong interface-interactions between the polyoxometalate and the UiO-66 framework.

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1. Introduction

Metal-organic frameworks (MOFs) are emerging as a class of crystalline porous materials with potential applications in gas adsorption [1,2], separation [3,4], magnetism [5], nonlinear optical properties [6], and catalysis [7,8]. Particularly, Zr-based metal-organic frameworks (ZrMOFs), which consist of $\text{Zr}^{\text{IV}}_6\text{O}_4(\text{OH})_4$ oxocluster nodes and organic linkers, attracted much attention mainly due to their significant stability. By using ZrMOF materials like UiO-66 and UiO-67 as catalysts or catalyst supports, a variety of highly efficient heterogeneous

ZrMOFs-based catalysts were developed for various catalytic reactions, including Lewis acid, oxidation, biomimetic, hydrogenation, electrocatalytic, and photocatalytic reactions [9–22].

It was reported that by immobilization of polyoxometalate (POM) clusters into Zr-based MOFs, hybrid POM@ZrMOF composites with controllable acidity, redox property, and catalytic performance were obtained [23–29]. In general, POM, including metal-substituted POM, were incorporated into MOFs via simple impregnation [30–32]. However, the supported POM catalysts prepared by this method usually suffer from low catalytic activity owing to the relatively low POM loading and

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nonuniform distribution of POM clusters. Moreover, POM leaching commonly occurs during the liquid-phase catalytic process mainly due to the instability of the large POM clusters on the solid support surfaces. Therefore, considerable efforts were devoted to developing more effective strategies to synthesize novel POM@MOFs hybrid composites with excellent catalytic activity and stability.

Recently, hybrid POM@MOF (including ZrMOF) composites were obtained by hydrothermal or solvothermal methods directly adding the POM (or precursors) as reactant to the MOF synthesis. For instance, Xie et al. [24] encapsulated 12-tungstophosphoric acid within the cage of UiO-66-2COOH by a one-pot solvothermal method, and then modified the hybrid composite with sulfonated acidic ionic liquids to create an efficient heterogeneous catalyst for converting acidic oil feedstock into biodiesel. Yang et al. [25] solvothermally synthesized a hybrid composite of $\text{PW}_{12}\text{@UiO-66}$, which exhibited high activity and reusability in the selective oxidation of cyclopentene to glutaraldehyde with H_2O_2 as the oxidant. Wang and co-authors [26,27] reported that hybrid composites involving phosphomolybdic acid and UiO-66 were obtained via a one-pot solvothermal method, and a synergistic effect between active Mo species and ZrMOF carriers was demonstrated contributing to a high oxidative desulfurization activity. POM@MOFs hybrid composites derived by this method showed a high dispersion of POM clusters into the matrices of the ZrMOFs support, excellent structure/chemical stability, as well as improved catalytic activity and recyclability caused by the effective interaction between POM and MOFs.

Previously, our group reported the synthesis of hybrid composites based on polyoxomolybdic cobalt (CoPMA) and UiO-67 or UiO-bpy (containing a bipyridine group) by the direct solvothermal method under optimized synthesis conditions [33]. The resultant CoPMA@UiO-bpy hybrid composite exhibited an excellent catalytic activity and stability for olefin epoxidation with H_2O_2 or O_2 /*tert*-butyl hydroperoxide as the oxidant. Here, we tried to extend the catalytic application for the family of POM@ZrMOFs composites using olefin epoxidation. Two types of hybrid composites composed of phosphomolybdate acid (PMo_{12}) and Co-substituted phosphomolybdate acid (PMo_{11}Co) units with UiO-66 MOFs were synthesized using the solvothermal method. The resultant POM@ZrMOFs hybrids were characterized by a variety of techniques, and their catalytic performance was investigated for the epoxidation of olefins with *tert*-butyl hydroperoxide as the oxidant. At the test conditions applied, $\text{PMo}_{11}\text{Co@UiO-66}$ showed a much higher catalytic activity than $\text{PMo}_{12}\text{@UiO-66}$. Moreover, this hybrid catalyst was recycled at least ten times without distinct

loss in catalytic activity.

2. Experimental

2.1. Materials

$\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, *N,N'*-dimethylformamide (DMF), diethyl ether, methanol, hydrochloric acid (37 wt%), chloroform, and phosphomolybdic acid (PMo_{12}) were purchased from Sinopharm Chemical Reagent Co., Ltd. ZrCl_4 , terephthalic acid (H_2BDC), styrene, 1-octene, 1-decene, cyclohexene, cyclooctene, cyclododecene, *cis*-stilbene, limonene and $5.5 \text{ mol} \cdot \text{L}^{-1}$ *tert*-butyl hydroperoxide (*t*-BuOOH) in *n*-decane were procured from Sigma-Aldrich. All the obtained chemicals were used without further purification.

2.2. Catalyst preparation

Co-substituted phosphomolybdic acid (PMo_{11}Co) with the formula $\text{H}_5\text{PMo}_{11}\text{O}_{39}\text{Co}_1 \cdot x\text{H}_2\text{O}$ was prepared according to literature [34]. The hybrid composites of PMo_{12} and PMo_{11}Co encapsulated in UiO-66 were synthesized based on a literature reported procedure to obtain pure UiO-66 [25]. Typically, ZrCl_4 (116 mg), H_2BDC (83 mg), 37 wt% hydrochloric acid (1250 μL) and PMo_{12} or PMo_{11}Co were dissolved in DMF (15 mL) and stirred for 1 h. The light green mixture was then transferred into a Teflon-lined stainless-steel autoclave and heated in an oven at 393 K for 24 h. After cooling down to room temperature, the blue precipitates were filtered, then extracted with ethanol in a Soxhlet apparatus for 24 h and dried under vacuum at 363 K overnight. The hybrid composites are denoted as $\text{PMo}_{12}\text{@UiO-66}$ and $\text{PMo}_{11}\text{Co@UiO-66}$, respectively, and the POM amounts loaded on these catalysts were determined by ICP-OES, as presented in Table 1.

For comparison, a reference catalyst named $\text{PMo}_{11}\text{Co/UiO-66-imp}$ was prepared by a conventional impregnation method. First, UiO-66 was synthesized according to a literature procedure [25]. Then, 100 mg of UiO-66 was added to 0.5 mL of a methanol solution of PMo_{11}Co ($12 \text{ mg} \cdot \text{mL}^{-1}$) at room temperature. After stirring for 2 h, the solids were separated by centrifugation and Soxhlet-extracted with methanol and then dried overnight under vacuum at 363 K to obtain the reference catalyst $\text{PMo}_{11}\text{Co/UiO-66-imp}$, respectively. The POM amount of this catalyst was determined by ICP-OES, as provided in Table 1.

2.3. Characterization

Table 1

Textural parameters derived from N_2 adsorption-desorption profiles as well as element compositions determined by ICP-OES analyses of various materials.

Sample	BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore diameter (nm)	POM loading ($\text{mmol} \cdot \text{g}^{-1} / \text{wt}\%$)	Mo loading ($\text{mmol} \cdot \text{g}^{-1} / \text{wt}\%$)	Co loading ($\text{mmol} \cdot \text{g}^{-1} / \text{wt}\%$)
UiO-66	1202	0.58	1.9	—	—	—
$\text{PMo}_{12}\text{@UiO-66}$	994	0.53	2.1	(0.040/7.3)	(0.480/4.6)	—
$\text{PMo}_{11}\text{Co@UiO-66}$	991	0.51	2.0	(0.038/6.7)	(0.418/4.0)	(0.038 / 0.2)
$\text{PMo}_{11}\text{Co/UiO-66-imp}$	956	0.47	1.9	(0.037/6.6)	(0.407/3.9)	(0.037 / 0.2)

X-ray powder diffraction (XRD) patterns were collected with a PANalytical B.V. Empyrean X-ray powder diffractometer. The morphology of the composite materials was measured by scanning electron microscopy (SEM) using a HITACHI SU-8020 electron microscope. Transmission electron microscopy (TEM) images were recorded on a JEM-2100F at an accelerating voltage of 200 kV equipped with an energy-dispersive spectroscopy analyzer. Thermogravimetry (TG) was carried out using a NETZSCH STA499F3, heating from 313 to 1173 K at a rate of 10 K min⁻¹ under air atmosphere. N₂ adsorption-desorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 automated adsorption analyzer. The surface areas were calculated using the BET (Brunauer-Emmett Teller) method. The pore size distributions were calculated by the NLDFT (non-linear density functional theory) method. Diffuse-reflectance UV-vis (DR-UV-vis) spectra were obtained with a Shimadzu-3600 UV-vis-NIR spectrophotometer. The Fourier-transform infrared (FT-IR) spectra were recorded on a NicoletTM 6700 spectrometer in the range of 4000 to 400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCA LAB 250Xi system with Al K α source. The measured spectra were referenced to the C 1s signal at 284.6 eV. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was carried out with an iCAP 7600 ICP instrument.

2.4. Catalytic tests

In a typical catalytic olefin epoxidation reaction, 1.0 mmol of olefin, 1.0 mmol of *t*-BuOOH, 3 mL of chloroform (solvent), and 10 mg of catalyst were added to a 10 mL round-bottomed flask equipped with a reflux condenser. The mixture was stirred for the required time at a specified temperature. The progress of the reaction was monitored using a Shimadzu GC-14C with a HP-5 capillary column. All the oxidation products were identified by comparison with standard samples and finally by gas chromatography-mass spectroscopy applying a GC-MS-QP 2010 plus. After reaction, the used catalyst was isolated by centrifugation and washed repeatedly with chloroform and methanol, and dried overnight at 363 K under vacuum.

3. Results and discussion

3.1. Synthesis and Characterization

The synthesis of the PMo₁₂@UiO-66 and PMo₁₁Co@UiO-66 hybrid composites was achieved through the in situ self-assembly of POM, ZrCl₄, and H₂BDC under solvothermal conditions. The typical synthesis is shown in Scheme 1. According to the coordination modulation mechanism of UiO-66 synthesis revealed in literature [26,27,35], various acids such as saturated monocarboxylic acid (e.g., acetic acid), benzoic acid, and hydrochloric acid could be used as modulator. In previous work [25], it was observed that POM@UiO-66 composites with controllable morphology and crystallinity could easily be obtained when hydrochloric acid was used as modulator. Therefore, the synthesis of PMo₁₂@UiO-66 and

Scheme 1. Typical synthesis of POM@UiO-66 composites.

PMo₁₁Co@UiO-66 was also achieved in the present work using hydrochloric acid as modulator.

Figure 1 shows the XRD patterns of the two POM@UiO-66 composites and UiO-66. The diffraction patterns of PMo₁₂@UiO-66 and PMo₁₁Co@UiO-66 match perfectly with the simulated pattern of UiO-66, confirming that the structure of the ZrMOF host is kept intact after incorporation of the POM units. The reference sample of PMo₁₁Co/UiO-66-imp shows also a similar XRD pattern as the parent UiO-66 (Fig. S1, ESI). Concerning the fact that these composites have relatively high POM loadings, with 7.3 wt% in PMo₁₂@UiO-66, 6.7 wt% in PMo₁₁Co@UiO-66, and 6.6 wt% in PMo₁₁Co/UiO-66-imp (Table 1), the absence of reflections originating from crystalline POMs or Co-related species are an indication that the introduced POMs (including Co species) are either highly dispersed within the MOF host or present in amorphous states.

The SEM images in Figs. 2(a)–(c) show the morphology of UiO-66, PMo₁₂@UiO-66, and PMo₁₁Co@UiO-66. Uniform spherical particles are observed in the images of the support and the hybrid composites. The fact that no noticeable change in morphology between UiO-66 and POM@UiO-66 occurred implies that the addition of POM units does not affect the crystal growth of the ZrMOFs [25].

The TEM images of PMo₁₁Co@UiO-66 are shown in Figs. 2(d) and 2(e). It is observed that this material is composed of irregular nanosized particles, and no distinct POM clusters are visible in Fig. 2(e). The energy dispersive spectrometry (EDS) mapping images, displayed in Figs. 2(g)–(i), reveal that Co, P

Fig. 1. XRD patterns of simulated UiO-66, UiO-66, and POM@UiO-66 composites.

Fig. 2. SEM images of UiO-66 (a), PMO₁₂@UiO-66 (b), and PMO₁₁Co@UiO-66 (c); (d,e) TEM images of PMO₁₁Co@UiO-66; (f) HAADF-STEM image of PMO₁₁Co@UiO-66; (g–i) EDS mapping images of PMO₁₁Co@UiO-66.

and Mo are evenly distributed in the PMO₁₁Co@UiO-66 composites. Therefore, it is proposed that the PMO₁₁Co clusters are uniformly encapsulated inside the cages of UiO-66.

The thermal stability of the hybrid composites, UiO-66, PMO₁₂@UiO-66, and PMO₁₁Co@UiO-66, was measured from room temperature to 1073 K using thermogravimetric (TG) analysis. As shown in Fig. 3, the TG curve of the UiO-66 sample exhibits two weight loss steps between 313 and 835 K. The first weight loss is attributed to the release of physically adsorbed water and guest DMF molecules. The further weight loss between 795 and 835 K is ascribed to the framework structure decomposition of MOFs. Further, the TG curve of PMO₁₂@UiO-66 and PMO₁₁Co@UiO-66 show a similar shape to that of UiO-66. Notably, the second weight loss at higher temperature corresponds to the decomposition of the UiO-66 framework and POM clusters into simple oxides. These results

Fig. 3. TG curves of UiO-66, PMO₁₂@UiO-66, and PMO₁₁Co@UiO-66.

suggest that both the UiO-66 support and POM@ZrMOF composites have excellent thermal stability, which is an important feature for catalytic applications [29,36,55].

The N₂ adsorption-desorption isotherms, the pore size distributions, and the textural parameters of hybrid composites are shown in Fig. 4, Fig. S2, and Table 1. All samples display a type I isotherm, indicating the microporous characteristic of these materials. The BET specific surface areas of UiO-66, PMO₁₂@UiO-66, and PMO₁₁Co@UiO-66 are 1202, 994 and 991 m²·g^{−1}, respectively. In addition, the pore volumes of PMO₁₂@UiO-66 and PMO₁₁Co@UiO-66 are 0.53 and 0.51 cm³·g^{−1}, respectively, lower than that of UiO-66 (0.58 cm³·g^{−1}), which indicates that POM units are distributed inside the cavities of the MOFs. Compared to PMO₁₁Co@UiO-66, the reference sample of PMO₁₁Co@UiO-66-imp exhibits a lower BET specific surface area (956 m²·g^{−1}) and pore volume (0.47 cm³·g^{−1}), possibly caused by the uneven distribution of POM clusters in the hybrid composite derived from the impregnation method.

The FT-IR spectra of PMO₁₂, PMO₁₁Co, UiO-66, and hybrid POM@UiO-66 composites are shown in Fig. 5. With respect to the PMO₁₂ spectrum, characteristic vibration bands appeared at 1065 (P=O), 966 (Mo=O), 869 (Mo–O_b–Mo), and 787 cm^{−1} (Mo–O_c–Mo), and are attributed to the Keggin structure of POM clusters [33]. The corresponding vibration bands of the

Fig. 4. (A) N₂ adsorption-desorption isotherms of UiO-66, PMO₁₂@UiO-66, and PMO₁₁Co@UiO-66 composites; (B) Pore size distribution curves of UiO-66, PMO₁₂@UiO-66, and PMO₁₁Co@UiO-66 composites.

Fig. 5. FT-IR spectra of PMo_{12} , PMo_{11}Co , UiO-66, and POM@UiO-66 composites.

PMo_{11}Co sample shifted slightly, which is an indication of the distortion induced by the introduced Co atoms. The observed vibration bands of the UiO-66 support and the hybrid composites between 1300 and 1750 cm^{-1} are mainly attributed to the carboxylate vibration of the organic linkers. In the FT-IR spectrum of POM@UiO-66, characteristic UiO-66 peaks are prominent and peaks corresponding to POM were insignificant as a result of the relatively low POM loading [25,31]. Notably, Wang and coauthors recently reported that weak IR and Raman signals related to PMo_{12} with Keggin structure were detected in the spectra of a hybrid material composed of phosphomolybdic acid and UiO-66, which was synthesized by a similar one-pot solvothermal method as adopted in this work [26,27]. Moreover, the presence of Keggin-type PMo_{12} clusters in the hybrid composite was further confirmed by combining the characterization results of ^{31}P NMR spectra, demonstrating that the basic POM structure remained intact after being incorporated into ZrMOFs using the solvothermal synthesis process [26,27].

Figure 6 depicts the DR-UV-vis spectra of PMo_{12} , PMo_{11}Co , UiO-66, and the hybrid composites. As observed in Fig. 6(A), PMo_{12} exhibits characteristic absorptions at about 217 and 313 nm, which were attributed to the charge transition from O^{2-} to Mo^{6+} in $\text{Mo}=\text{O}$ and $\text{Mo}-\text{O}-\text{Mo}$ bonds. PMo_{11}Co presents a spectrum similar to that of PMo_{12} mainly due to the resemblance of these two materials with respect to structure and composition. A slightly blue-shift of PMo_{11}Co was detected, suggesting that

the incorporation of a small cobalt amount into the primary structure of PMo_{12} resulted in a subtle change in the chemical environment of the Mo species [37]. From Fig. 6(B), it was observed that the UiO-66 support shows a maximum UV absorption λ_{max} at 239 nm, with an absorption edge extended up to 320 nm. Compared to UiO-66, the spectra of the hybrid composites present an extra shoulder at approximately 300–400 nm, which is related to the presence of Mo^{VI} species in the hybrid composites [38]. Moreover, the broad adsorption in the range of 600–800 nm corresponded to $d-d$ transitions of Mo^{V} species in octahedral coordination, implying that a part of the Mo^{VI} species were reduced to Mo^{V} species during the formation of the hybrid POM@UiO-66 composites [27].

The Mo 3d XPS profiles of PMo_{12} , PMo_{11}Co , and POM@UiO-66 hybrid composites are displayed in Fig. 7(A). For PMo_{12} , the appearance of binding energies at 236.4 and 233.3 eV are attributed to the $\text{Mo}^{\text{VI}} 3d_{3/2}$ and $\text{Mo}^{\text{VI}} 3d_{5/2}$, respectively [33,34,39–42]. The binding energies of Mo 3d in PMo_{11}Co were slightly negative shifted (236.2 and 233.1 eV). As for the hybrid composite of $\text{PMo}_{11}\text{Co}@ \text{UiO-66}$, the binding energies of Mo 3d showed a more negative shift (235.7 and 232.6 eV), indicating that a partial electron transfer occurred from the UiO-66 frameworks to the POM clusters [34]. Similar results were reported by Wang and co-workers, and they reported that a small amount of Mo^{V} species (binding energy at 231.2 eV) may be formed in PMA/UiO-66 composites (PMA = PMo_{12}) due to the presence of strong metal-support interactions (SMSIs) between the PMA and UiO-66 framework [26,27]. In our case, the deconvolution of the Mo 3d XPS profiles of $\text{PMo}_{12}@ \text{UiO-66}$ and $\text{PMo}_{11}\text{Co}@ \text{UiO-66}$ did not generate distinct Mo^{V} signals, indicating that Mo^{VI} species are still predominant in this hybrid composite, whereas only trace amounts of Mo^{V} species might be present at the interface between POM clusters and the UiO-66 framework. As shown in Fig. 7(B), the XPS profiles of Co 2p for PMo_{11}Co present two main peaks centered at around 795.5 and 780.2 eV, which were ascribed to $\text{Co}^{\text{II}} 2p_{1/2}$ and $\text{Co}^{\text{II}} 2p_{3/2}$, respectively [43–45,53,54]. The Co 2p signals of $\text{PMo}_{11}\text{Co}@ \text{UiO-66}$ exhibited a slightly negative shift (795.1 and 779.8 eV) compared to those of PMo_{11}Co , thus providing further evidence that the chemical environments of the Co substituted POM units change to some extent after being introduced

Fig. 6. (A) DR-UV-vis spectra of PMo_{12} and PMo_{11}Co ; (B) DR-UV-vis spectra of UiO-66 and POM@UiO-66 composites.

Fig. 7. (A) XPS profiles for the binding energies of Mo 3d in PMo_{12} , PMo_{11}Co , $\text{PMo}_{11}\text{Co@UiO-66}$, and reused $\text{PMo}_{11}\text{Co@UiO-66}$; (B) XPS profiles for the binding energies of Co 2p in PMo_{11}Co , $\text{PMo}_{11}\text{Co@UiO-66}$, and reused $\text{PMo}_{11}\text{Co@UiO-66}$.

into the ZrMOFs due to the presence of host-guest interactions. These results suggest that the oxidation states of Mo and Co were only moderately reduced after the POM units were encapsulated into the framework of UiO-66, mainly due to the existence of relatively strong metal-support interactions, which led to a partial electron transfer from the UiO-66 frameworks to POM units.

3.2. Catalytic performance of POM@UiO-66 composites

The catalytic properties of the POM@UiO-66 composites were first investigated for the epoxidation of cyclooctene with *t*-BuOOH as the oxidant in the presence of chloroform as the solvent (Table 2 and Fig. S3). Both $\text{PMo}_{12}\text{@UiO-66}$ and $\text{PMo}_{11}\text{Co@UiO-66}$ catalyze the epoxidation of cyclooctene, whereas a relatively higher catalytic activity was observed for the Co-substituted catalyst sample. Based on the calculated TOF values of various catalysts listed in Table 2, it is observed that the activity of $\text{PMo}_{11}\text{Co@UiO-66}$ (TOF 19 h^{-1} at 334 K) is comparable to that of POM-based catalysts like $\text{Mo}(\text{CO})_3\text{-L@UiO-66}$ (TOF 19 h^{-1} at 353 K) reported in literature, but is lower than that of our previously reported $\text{PMo}_{12}\text{@COF-300}$ (TOF 44 h^{-1} at 334 K) [40,46,47]. It should be mentioned that the reference

catalyst $\text{PMo}_{11}\text{Co@UiO-66-imp}$, prepared by the impregnation method, is also reasonably active for the epoxidation reaction (Fig. S4). However, this catalyst is not stable at the test condition, serious leaching of POM species was detected during the reaction (Fig. S5). $\text{PMo}_{11}\text{Co@UiO-66}$ provided a much higher stability against leaching proven by a hot filtration experiment, demonstrating the true heterogeneous nature of this hybrid catalyst (Fig. 8). Additional experiments demonstrated that $\text{PMo}_{11}\text{Co@UiO-66}$ was easily recycled by simple filtration, washing with chloroform and drying at 363 K. The catalytic activity was nearly unchanged after the tenth run, indicating the excellent recyclability of the catalyst.

The high stability of $\text{PMo}_{11}\text{Co@UiO-66}$ was confirmed by further characterization of the used catalysts, including XRD, FT-IR, DR-UV-vis and XPS (Fig. S6–S8). There were no significant differences in the spectra between the fresh and the used catalyst. The appearance of weak vibrations at 2948 and 2859 cm^{-1} in the FT-IR spectrum of the used catalyst was attributed to the existence of a small amount of reactants or products adsorbed on the surface of the used $\text{PMo}_{11}\text{Co@UiO-66}$ catalyst. Notably, the broad absorption peak in the range of 600–800 nm in the DR-UV-vis spectrum of the fresh $\text{PMo}_{11}\text{Co@UiO-66}$ catalyst disappeared after the catalytic test, which was also

Table 2

Cyclooctene epoxidation performance of various catalyst samples^a.

Entry	Catalyst	Amount of catalyst (mg)	Time (h)	Conversion (%)	TOF ^b (h^{-1})	Related work
1	Blank	—	6	3	—	This work
2	UiO-66	10	6	3	—	This work
3	$\text{PMo}_{12}\text{@UiO-66}$	10	6	32	11	This work
4	$\text{PMo}_{11}\text{Co@UiO-66}$	10	6	52	19 ^c	This work
5	$\text{PMo}_{11}\text{Co@UiO-66-imp}$	10	6	40	15 ^c	This work
6	$\text{PMo}_{12}\text{@COF-300}$ ^f	10	3	63	44	[40]
7	$\text{Mo}(\text{CO})_3\text{-L@UiO-66}$ ^d	100	4.5	98	19	[46]
8	$\text{PMo}_{12}\text{@meso-organosilicates}$ ^e	100	6	58	4	[47]

^a Reaction condition: olefin 1.0 mmol, *t*-BuOOH 1.0 mmol, chloroform 3 mL, reaction temperature 334 K.

^b TOF is expressed in $\text{mol}(\text{cyclooctene})\cdot\text{mol}(\text{Mo})^{-1}\cdot\text{h}^{-1}$.

^c TOF is expressed in $\text{mol}(\text{cyclooctene})\cdot\text{mol}(\text{Mo \& Co})^{-1}\cdot\text{h}^{-1}$.

^d Reaction condition: cyclooctene 1.0 mmol, *t*-BuOOH 2.0 mmol, acetonitrile 3 mL, reaction temperature 353 K.

^e Reaction condition: cyclooctene 5.0 mmol, *t*-BuOOH 5.0 mmol, *n*-dodecane 5.0 mmol (internal standard), chloroform 10 mL, reaction temperature 323 K.

^f Reaction condition: cyclooctene 1.0 mmol, *t*-BuOOH 1.0 mmol, chloroform 2 mL, reaction temperature 334 K.

Fig. 8. Leaching (A) and recycling (B) experiments of $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$. Reaction conditions: cyclooctene 5.0 mmol, *t*-BuOOH 5.0 mmol, $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ 50 mg, solvent 15 ml, 334 K, 6 h. All epoxide selectivity was greater than 99%.

related to the adsorption of reactants/products on the surface of the used $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ catalyst [34].

The influence of solvents on the catalytic properties of $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ was investigated by testing different solvents for the epoxidation reaction. As shown in Fig. 9, the catalytic activity of $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ is solvent-dependent, decreasing in the order of tetrachloromethane $\approx$ chloroform > toluene > acetonitrile > ethanol. It was proposed that highly coordinating solvents such as acetonitrile and ethanol may considerably decrease the catalytic activity, since they compete with *t*-BuOOH to bind to the metal centers [57–59]. Besides, the relatively strong polarity of these solvents easily entrap them in the polar channel/cavity of UiO-66, thus considerably decrease the accessibility of the reagents to the encapsulated POM sites (olefin and *t*-BuOOH), finally resulting in a poor activity (even no reactivity) of the hybrid $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ catalyst. Hereafter, chloroform was chosen as solvent to further study the catalytic property of $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ for the epoxidation of other olefins.

Additional experiments showed that $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ is also catalytically active for epoxidizing cyclooctene with H_2O_2 as the oxidant (Table S1). However, this catalyst was unstable at

Fig. 9. Solvent effect on cyclooctene epoxidation. Reaction conditions: cyclooctene 1.0 mmol, *t*-BuOOH 1.0 mmol, $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ 10 mg, solvent 3 ml, 334 K, 6 h. Selectivity for the epoxide is greater than 99%.

the tested condition, and leaching of active species was detected because of the strong complexing capability of H_2O_2 . This feature differed from our previously reported $\text{CoPMA}@ \text{UiO}-\text{bpy}$ catalyst, which was active and stable with respect to the H_2O_2 -mediated epoxidation reaction [33]. These results suggested that changing the bridged ligands in ZrMOFs considerably affected the catalytic performance of the $\text{POM}@ \text{ZrMOF}$ catalysts.

As shown in Table 3, $\text{PMo}_{11}\text{Co}@ \text{UiO}-66$ is catalytically active for the epoxidation of a wide range of olefins, including various cyclic and linear olefins. Of these, linear olefins like 1-octene and 1-decene were converted to the corresponding epoxides at relative low conversion. Cyclic olefins such as cyclohexene and cyclododecene were oxidized at higher conversions. However, more side products like aldehydes, enols, and ketenes were

Table 3
Epoxidation of olefins catalyzed by $\text{PMo}_{11}\text{Co}@ \text{UiO}-66^a$.

Entry	Olefin	Epoxide	Conversion ^c (%)	Selectivity ^c (%)	TOF (h ⁻¹)
1 ^b			55	69 ^d	10
2			68	>99	12
3			61	71 ^d	11
4			63	74 ^d	12
5	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}_2$		16	>99	3
6	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}_2$		12	>99	2
7			42	69 ^d	8

^a Reaction conditions: olefin 1 mmol, *t*-BuOOH 1 mmol, catalyst 10 mg, chloroform 3 mL, reaction temperature 334 K, and reaction time 12 h.

^b 1.0 mmol chlorobenzene was added as internal standard.

^c Conversion and selectivity were determined by GC-MS.

^d By products like aldehydes, enol, ketene, etc.; see Scheme S1.

^e TOF is expressed in $\text{mol}(\text{olefin}) \cdot \text{mol}(\text{Mo \& Co})^{-1} \cdot \text{h}^{-1}$.

Fig. 10. Conversion and selectivity during selective limonene oxidation. Reaction conditions: limonene 10 mmol, *t*-BuOOH 20 mmol, catalyst 100 mg, chloroform 30 mL, reaction temperature 334 K.

detected (Scheme S1). $\text{PMo}_{11}\text{Co@UiO-66}$ is also active for the epoxidation of *cis*-stilbene showing 42% conversion and 69% selectivity. The formation of multiple side products implies that various catalytic oxidation pathways are possible, as discussed later.

The epoxidation of limonene was investigated to further understand the nature of the active sites of $\text{PMo}_{11}\text{Co@UiO-66}$ and the main paths of the oxidation reactions (see Fig. 10). Limonene has two types of double bonds, making it an ideal compound to reveal the catalytic mechanism. As shown in Scheme 2, various products including 1,2-limonene oxide, limonene dioxide, carveol, carvone, and perillyl alcohol were formed in the catalytic limonene oxidation, which are highly dependent on the nature of the active sites of the catalysts as well as the operating conditions. As shown in Fig. 10, a relative high selectivity (64%) to 1,2-limonene oxide, the most valuable product, was achieved over $\text{PMo}_{11}\text{Co@UiO-66}$ at the tested condition. In terms of regioselectivity, the 1,2-C=C double bond is much easier oxidized to form the oxirane ring than the 8,9-C=C double bond, suggesting that the oxygen transfer preferentially takes place at the electron-rich endocyclic position [48–51].

In general, a peroxidic oxygen donor such as *t*-BuOOH might be directly activated by Mo-containing POM catalysts to form a Mo-OOR adduct, which is regarded as an active intermediate generating the epoxide (path 1). Besides, the peroxidic oxygen donor might also be homolytically activated to form a radical species, which can result in the formation of allylic oxidation products (path 2) [52]. In the present case, the

Scheme 2. Main products of selective limonene oxidation.

$\text{PMo}_{11}\text{Co@UiO-66}$ catalyst exhibits a considerable high selectivity to both the epoxides and the allylic oxidation products oxidizing cyclic olefins like limonene, revealing that the two catalytic oxidation pathways (path 1 and path 2) are competitive, as described in Scheme 3.

Further control experiments showed that the limonene oxidation over $\text{PMo}_{11}\text{Co@UiO-66}$ was partially inhibited if hydroquinone was introduced as a radical scavenger. In this case (Figs. S9 and S10), the limonene conversion slightly decreased (i.e., from 22% to 13% after 2 h of reaction), while the selectivity to epoxides significantly increased (from 44% to 91%). These results provided strong evidence that the homolytic radical-mediated pathway was indeed active in the olefin oxidation process, which can be prevented by introducing a radical scavenger.

Previously, it was reported that the substitution of phosphomolybdic acid by transition metals (TMs) like Ti, V, Co, Nb, and Rh considerably improves the catalytic oxidation ability of the POM catalysts [33,34,51–54]. Introducing a small amount of transition metals might adjust the electron density of the neighboring Mo species forming TM–O–Mo bonds, thus activating the olefin epoxidation activity [34]. Moreover, recent literature work that combined a variety of characterization results with DFT calculations revealed that substituted transition metals such as Ti or Nb can act as a new active site to directly activate oxidants like *t*-BuOOH and H_2O_2 [56,60,61]. In our case, the electron density of Mo atoms in POM decreased slightly after introducing a small amount of Co, as suggested by the XPS results. Meanwhile, the chemical environments of the Co atoms changed too, due to the formation of Co–O–Mo bonds. Therefore, it is proposed that the relatively high catalytic activity of $\text{PMo}_{11}\text{Co@UiO-66}$ compared to that of $\text{PMo}_{12}\text{@UiO-66}$ is mainly attributed to the formation of Co-containing active sites (i.e., Co–O–Mo species), which directly activate *t*-BuOOH to produce highly active hydroperoxo species.

By comparing the catalytic properties of the solvothermally synthesized $\text{PMo}_{11}\text{Co@UiO-66}$ and $\text{PMo}_{11}\text{Co/UiO-66-imp}$ prepared by the impregnation-method (Table 2 and Fig. S4), it was determined that the POM units dispersed on the surface were not stable during the liquid-phase catalytic oxidation process, whereas the confined POM units in the UiO-66 cage provided a much higher stability against active site leaching. Based on literature and our previous work [25,33], the high stability of $\text{PMo}_{11}\text{Co@UiO-66}$ was mainly attributed to the spatial confinement of the PMo_{11}Co units within the cages of the UiO-66

Scheme 3. Proposed oxygen activation mechanism of *t*-BuOOH.

frameworks. Given the size of PMo_{11}Co (about 10 Å), it just fits the size of the superoctahedral cages (11 Å) of the UiO-66 MOFs. Therefore, the octahedral cages with smaller triangular windows (5–7 Å) can encapsulate the POM units, and effectively prevent the loss of POM during the catalytic tests. Interactions between POM units and the UiO-66 frameworks, as proven by XPS characterization results, also play a positive role in generating a highly stable hybrid composite catalyst.

On other hand, the window of the UiO-66 framework is big enough to allow reactants and products to enter or exit the cage, which means that the POM active sites located inside the cage of MOFs are easily accessible for the catalytic reaction. Other factors, such as the surface polarity of the POM@ZrMOF catalysts are also quite important to achieve a high catalytic performance, which polarity can significantly influence the diffusion of reactants/products. It seems that the $\text{PMo}_{11}\text{Co@UiO-66}$ polarity is beneficial for the olefin epoxidations with *t*-BuOOH as the oxidant using chloroform as a solvent.

4. Conclusions

In this work, the hybrid composites of $\text{PMo}_{11}\text{Co@UiO-66}$ and $\text{PMo}_{12}\text{@UiO-66}$ were synthesized by a one-pot solvothermal method. Characterization results demonstrated that the primary crystalline structure of the UiO-66 support remains intact after introducing POM into the cages of the MOF supports. Relatively strong metal-support interactions are present between the POM units and UiO-66 frameworks. The $\text{PMo}_{11}\text{Co@UiO-66}$ catalyst shows excellent catalytic activity, selectivity, and stability during the epoxidation of a variety of olefins with *t*-BuOOH as the oxidant. The UiO-66 framework stabilizes the incorporated PMo_{11}Co units by spatial confinement as well as by the interaction between the POM units and the ZrMOF framework. Further work is currently underway to study the catalytic performance of these hybrid composites for molecular oxygen-mediated olefin epoxidation reactions in order to extend their catalytic application in oxidation processes.

Conflict of Interest

The authors declare no conflict of interest.

References

- [1] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science*, **2002**, 295, 469–472.
- [2] J. W. Yoon, S. H. Jhung, Y. K. Hwang, S. M. Humphrey, P. T. Wood, J. S. Chang, *Adv. Mater.*, **2007**, 19, 1830–1834.
- [3] J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.*, **2009**, 38, 1477–1504.
- [4] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature*, **2005**, 436, 238–241.
- [5] G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science*, **2002**, 298, 1762–1765.
- [6] O. R. Evans, W. Lin, *Acc. Chem. Res.*, **2002**, 35, 511–522.
- [7] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C. Y. Su, *Chem. Soc. Rev.*, **2014**, 43, 6011–6061.
- [8] L. Jiao, Y. Wang, H. L. Jiang, Q. Xu, *Adv. Mater.*, **2018**, 30, e1703663.
- [9] S. T. Gao, W. Liu, C. Feng, N. Z. Shang, C. Wang, *Catal. Sci. Technol.*, **2016**, 6, 869–874.
- [10] L. Shen, W. Wu, R. Liang, R. Lin, L. Wu, *Nanoscale*, **2013**, 5, 9374–9382.
- [11] C. S. Hinde, W. R. Webb, B. K. Chew, H. R. Tan, W. H. Zhang, T. S. Hor, R. Raja, *Chem. Commun.*, **2016**, 52, 6557–6560.
- [12] J. C. Wang, Y. H. Hu, G. J. Chen, Y. B. Dong, *Chem. Commun.*, **2016**, 52, 13116–13119.
- [13] M. Kaposi, M. Cokoja, C. H. Hutterer, S. A. Hauser, T. Kaposi, F. Klappenberger, A. Pothig, J. V. Barth, W. A. Herrmann, F. E. Kuhn, *Dalton Trans.*, **2015**, 44, 15976–15983.
- [14] L. Chen, R. Luque, Y. Li, *Dalton Trans.*, **2018**, 47, 3663–3668.
- [15] F. Zhang, S. Zheng, Q. Xiao, Y. Zhong, W. Zhu, A. Lin, M. Samy El Shall, *Green Chem.*, **2016**, 18, 2900–2908.
- [16] M. W. Logan, Y. A. Lau, Y. Zheng, E. A. Hall, M. A. Hettinger, R. P. Marks, M. L. Hosler, F. M. Rossi, Y. Yuan, F. J. Uribe-Romo, *Catal. Sci. Technol.*, **2016**, 6, 5647–5655.
- [17] R. Insyani, D. Verma, S. M. Kim, J. Kim, *Green Chem.*, **2017**, 19, 2482–2490.
- [18] J. Chen, K. Li, L. Chen, R. Liu, X. Huang, D. Ye, *Green Chem.*, **2014**, 16, 2490–2499.
- [19] H. G. T. Nguyen, L. Mao, A. W. Peters, C. O. Audu, Z. J. Brown, O. K.

Graphical Abstract

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Solvothermal synthesis of Co-substituted phosphomolybdate acid encapsulated in the UiO-66 framework for catalytic application in olefin epoxidation

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Hybrid composites based on Co-substituted phosphomolybdic acid (PMo_{11}Co) and UiO-66 were synthesized by the direct solvothermal method. $\text{PMo}_{11}\text{Co@UiO-66}$ showed high catalytic activity and stability for the epoxidation of a variety of olefins with *t*-BuOOH as the oxidant.

- Farha, J. T. Hupp, S. T. Nguyen, *Catal. Sci. Technol.*, **2015**, 5, 4444–4451.
- [20] A. H. Valekar, K. H. Cho, S. K. Chitale, D. Y. Hong, G. Y. Cha, U. H. Lee, D. W. Hwang, C. Serre, J. S. Chang, Y. K. Hwang, *Green Chem.*, **2016**, 18, 4542–4552.
- [21] M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. D. Vos, N. Stock, *Chem. Commun.*, **2015**, 51, 12578–12581.
- [22] F. Nouar, M. I. Breeze, B. C. Campo, A. Vimont, G. Clet, M. Daturi, T. Devic, R. I. Walton, C. Serre, *Chem. Commun.*, **2015**, 51, 14458–14461.
- [23] A. Dhakshinamoorthy, A. Santiago-Portillo, A. M. Asiri, H. Garcia, *ChemCatChem*, **2019**, 11, 899–923.
- [24] W. Xie, F. Wan, *Chem. Eng. J.*, **2019**, 365, 40–50.
- [25] X. L. Yang, L. M. Qiao, W. L. Dai, *Microporous Mesoporous Mater.*, **2015**, 211, 73–81.
- [26] X. M. Zhang, Z. Zhang, B. Zhang, X. Yang, X. Chang, Z. Zhou, D. H. Wang, M. H. Zhang, X. H. Bu, *Appl. Catal. B*, **2019**, 256, 117804.
- [27] X. Chang, X. F. Yang, Y. Qiao, S. Wang, M. H. Zhang, J. Xu, D. H. Wang, X. H. Bu, *Small*, **2020**, DOI: 10.1002/sml.201906432, 1906432.
- [28] C. T. Buru, P. Li, B. L. Mehdi, A. Dohnalkova, A. E. P. Prats, N. D. Browning, K. W. Chapman, J. T. Hupp, O. K. Farha, *Chem. Mater.*, **2017**, 29, 5174–5181.
- [29] W. Salomon, C. Roch-Marchal, P. Mialane, P. Rouschmeyer, C. Serre, M. Haouas, F. Taulelle, S. Yang, L. Ruhlmann, A. Dolbecq, *Chem. Commun.*, **2015**, 51, 2972–2975.
- [30] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science*, **2005**, 309, 2040–2042.
- [31] W. Salomon, F. J. Yazigi, C. Roch-Marchal, P. Mialane, P. Horcajada, C. Serre, M. Haouas, F. Taulelle, A. Dolbecq, *Dalton Trans.*, **2014**, 43, 12698–12705.
- [32] N. V. Maksimchuk, O. A. Kholdeeva, K. A. Kovalenko, V. P. Fedin, *Isr. J. Chem.*, **2011**, 51, 281–289.
- [33] X. Song, D. Hu, X. Yang, H. Zhang, W. Zhang, J. Li, M. Jia, J. Yu, *ACS Sustain. Chem. Eng.*, **2019**, 7, 3624–3631.
- [34] X. Song, W. Zhu, K. Li, J. Wang, H. Niu, H. Gao, W. Gao, W. Zhang, J. Yu, M. Jia, *Catal. Today*, **2016**, 259, 59–65.
- [35] A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, *Chem. Eur. J.*, **2011**, 17, 6643–6651.
- [36] B. Tu, Q. Pang, H. Xu, X. Li, Y. Wang, Z. Ma, L. Weng, Q. Li, *J. Am. Chem. Soc.*, **2017**, 139, 7998–8007.
- [37] J. She, Z. Fu, J. Li, B. Zeng, S. Tang, W. Wu, H. Zhao, D. Yin, S. R. Kirk, *Appl. Catal. B*, **2016**, 182, 392–404.
- [38] N. Afzali, R. Kardanpour, F. Zadehahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, A. Mechler, I. M. Baltork, M. Bahadori, *Appl. Organomet. Chem.*, **2019**, 33, e5225.
- [39] X. Song, Y. Yan, Y. Wang, D. Hu, L. Xiao, J. Yu, W. Zhang, M. Jia, *Dalton Trans.*, **2017**, 46, 16655–16662.
- [40] W. Gao, X. Sun, H. Niu, X. Song, K. Li, H. Gao, W. Zhang, J. Yu, M. Jia, *Microporous Mesoporous Mater.*, **2015**, 213, 59–67.
- [41] X. Song, W. Zhu, Y. Yan, H. Gao, W. Gao, W. Zhang, M. Jia, *J. Mol. Catal. A*, **2016**, 413, 32–39.
- [42] X. Song, W. Zhu, Y. Yan, H. Gao, W. Gao, W. Zhang, M. Jia, *Microporous Mesoporous Mater.*, **2017**, 242, 9–17.
- [43] C. Qin, A. Fan, D. Ren, C. Luan, J. Yang, Y. Liu, X. Zhang, X. Dai, M. Wang, *Electrochim. Acta*, **2019**, 323, 134756.
- [44] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. S. C. Smart, *Appl. Surf. Sci.*, **2011**, 257, 2717–2730.
- [45] Q. Zhang, J. Zhang, H. Yang, Y. Dong, Y. Liu, L. Yang, D. Wei, W. Wang, L. Bai, H. Chen, *Catal. Sci. Technol.*, **2019**, 9, 2915–2922.
- [46] N. Afzali, S. Tangestaninejad, M. Moghadam, V. Mirkhani, A. Mechler, I. Mohammadpoor-Baltork, R. Kardanpour, F. Zadehahmadi, *Appl. Organomet. Chem.*, **2018**, 32, e3958.
- [47] J. Wang, Y. Zou, Y. Sun, M. Hemgesberg, D. Schaffner, H. Gao, X. Song, W. Zhang, M. Jia, W. R. Thiel, *Chin. J. Catal.*, **2014**, 35, 532–539.
- [48] A. Gallo, C. Tiozzo, R. Psaro, F. Carniato, M. Guidotti, *J. Catal.*, **2013**, 298, 77–83.
- [49] S. Lwin, Y. Li, A. I. Frenkel, I. E. Wachs, *ACS Catal.*, **2016**, 6, 3061–3071.
- [50] X. Carrier, E. Marceau, H. Carabineiro, V. Rodriguez-Gonzalez, M. Che, *Phys. Chem. Chem. Phys.*, **2009**, 11, 7527–7539.
- [51] C. Bisio, A. Gallo, R. Psaro, C. Tiozzo, M. Guidotti, F. Carniato, *Appl. Catal. A*, **2019**, 581, 133–142.
- [52] J. Hu, K. Li, W. Li, F. Ma, Y. Guo, *Appl. Catal. A*, **2009**, 364, 211–220.
- [53] J. Liu, T. Chen, P. Jian, L. Wang, *Chin. J. Catal.*, **2018**, 39, 1942–1950.
- [54] J. Liu, R. Meng, J. Li, P. Jian, L. Wang, R. Jian, *Appl. Catal. B*, **2019**, 254, 214–222.
- [55] J. Hafizovic Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.*, **2008**, 130, 13850–13851.
- [56] C. Ci, H. Liu, L. Yan, Z. Su, *ChemistryOpen*, **2016**, 5, 470–476.
- [57] M. Bagherzadeh, L. Tahsini, R. Latifi, L. K. Woo, *Inorg. Chim. Acta*, **2009**, 362, 3698–3702.
- [58] M. Bagherzadeh, M. Zare, V. Amani, A. Ellern, L. Keith Woo, *Polyhedron*, **2013**, 53, 223–229.
- [59] F. Payami, A. Bezaatpour, H. Eskandari, *Appl. Organomet. Chem.*, **2018**, 32, e3986.
- [60] P. Jiménez-Lozano, I. Y. Skobelev, O. A. Kholdeeva, J. M. Poblet, J. J. Carbó, *Inorg. Chem.*, **2016**, 55, 6080–6084.
- [61] N. V. Maksimchuk, G. M. Maksimov, V. Y. Evtushok, I. D. Ivanchikova, Y. A. Chesalov, R. I. Maksimovskaya, O. A. Kholdeeva, A. Solé-Dauria, J. M. Poblet, J. J. Carbó, *ACS Catal.*, **2018**, 8, 9722–9737.

溶剂热法合成UiO-66金属有机框架限域的钴取代磷钼酸及其催化烯烃环氧化性能

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摘要: 金属有机框架材料是一类新型晶体孔性材料, 在气体储存、物质分离、非线性光学及催化等领域中具有潜在应用价值。其中, 基于钼氧簇和有机配体构筑的钼基金属有机框架材料(ZrMOFs)因其具有更高的结构稳定性而备受关注。研究表明, 将多金属钼酸盐(POM)负载在ZrMOFs载体上能够获得一类新型复合材料催化剂。这类材料具有可调控的酸性和氧化还原性, 已在一些固体酸催化及选择氧化(包括烯烃环氧化)等反应中表现出优异的催化性能。

多金属钼酸盐通常可以通过简单的浸渍法引入到ZrMOFs载体上, 但这种方法制备的催化剂普遍存在活性组分分散不均匀且易于在液相催化反应过程中发生活性组分流失的问题。因此, 当前的研究重点主要集中在如何通过简单有效的制

备方法获得结构更加稳定、性能更加优异的复合材料催化剂。近期,国内外多个研究小组分别报道了采用溶剂热法能够一步合成出POM@ZrMOFs复合材料,这类材料的主要特点是POM团簇能够均匀的分散在ZrMOFs孔道中,从而使其在氧化脱硫及烯烃选择氧化等反应中表现出更高的稳定性。考虑到POMs及ZrMOFs种类和结构的多样性,可以预期这类复合材料的合成及催化性能研究仍有很大的发展空间。

本文采用溶剂热法将磷钼酸(PMo_{12})及钴取代磷钼酸(PMo_{11}Co)限域在一类ZrMOFs材料(UiO-66)的孔道中,得到了两种复合材料催化剂,分别记为 $\text{PMo}_{12}@UiO-66$ 和 $\text{PMo}_{11}\text{Co}@UiO-66$ 。通过以叔丁基过氧化氢($t\text{-BuOOH}$)为氧化剂烯烃环氧化反应考察了其催化性能。相较于 $\text{PMo}_{12}@UiO-66$,含有钴取代磷钼酸的 $\text{PMo}_{11}\text{Co}@UiO-66$ 杂化材料表现出了更高的催化活性和稳定性。催化剂经简单的过滤和洗涤后即可循环使用多次,且催化性能基本保持不变。值得一提的是, $\text{PMo}_{11}\text{Co}@UiO-66$ 对多种类型烯烃的环氧化反应均表现出较高的催化活性和环氧选择性。例如,在加入自由基抑制剂对二苯酚后,柠檬烯选择性氧化为柠檬烯-1,2-环氧化物的选择性可以达到91%,性能明显优于文献中报道的其它类型催化剂。此外,溶剂种类对 $\text{PMo}_{11}\text{Co}@UiO-66$ 的催化活性有着显著的影响,在极性相对较强的乙醇、乙腈等溶剂中,催化剂的活性较低;在极性较弱的甲苯、氯仿,四氯化碳等溶剂中,催化剂的活性则相对较高。溶剂极性的差异会影响反应物分子与催化剂活性中心的接触情况,继而对催化剂的活性产生较大影响。

采用X射线衍射、氮吸附-脱附、X射线光电子能谱、傅立叶变换红外光谱(FT-IR)等手段对催化反应前后的 $\text{PMo}_{11}\text{Co}@UiO-66$ 催化剂进行了表征。结果表明,在溶剂热法合成的杂化材料催化剂中,引入的POM团簇能够均匀的分散在UiO-66框架材料的孔道和笼中;催化剂反应前后的组成与结构没有发生明显的变化。结合相关文献报道的结果,可以认为杂原子Co的引入能够产生类似于Co–O–Mo的新的活性中心,从而使 $\text{PMo}_{11}\text{Co}@UiO-66$ 表现出更高的催化活性。催化剂的高稳定性应主要归因于UiO-66框架对 PMo_{11}Co 团簇的空间限域作用。这种空间限域作用能够使 PMo_{11}Co 团簇被封装在UiO-66的八面体笼中,且二者之间还存在着较强的金属-载体间相互作用。在后续的工作中,我们还将继续深入研究 $\text{PMo}_{11}\text{Co}@UiO-66$ 催化剂的活性中心性质及其对分子氧的活化能力,加深对催化作用机制等问题的理解,进一步扩大这类复合材料催化剂的应用范围。

关键词: 多金属氧酸盐; 金属有机框架; 烯烃; 环氧化; 溶剂热合成

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