FULL PAPER

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Dodecatungstocobaltate heteropolyanion encapsulation into MIL-101(Cr) metal–organic framework scaffold provides a highly efficient heterogeneous catalyst for methanolysis of epoxides

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A heterogeneous catalyst was synthesized by encapsulation of a Keggin-type heteropolytungstate, potassium dodecatungstocobaltate trihydrate, $K_5[CoW_{12}O_{40}] \cdot$(Co-POM), into chromium(III) terephthalate (MIL-101). Encapsulation was achieved via a 'build bottle around ship' strategy in aqueous media, following a hydrothermal method. The structure of the resulting crystalline solid was characterized using X-ray diffraction, correlated with Fourier transform infrared and UV–visible spectroscopy. The metal content was analysed using optical emission spectroscopy. Transmission electron microscopy was used to measure particle size and N_2 adsorption in a Brunauer–Emmett–Teller instrument to characterize the specific surface area. The catalytic activity was investigated using methanolysis of epoxides under mild conditions as a test reaction. The turnover frequency of the heterogeneous Co-POM@MIL-101 catalyst was more than 20 times higher than that of the homogeneous Co-POM catalyst. The Co-POM@MIL-101 catalyst was reused several times with negligible leaching of Co-POM and with no considerable loss of its initial efficiency. The simplicity of preparation, extraordinary stability and high reactivity make Co-POM@MIL-101 an exceptional catalytic matrix that is easily separable from reaction media.

KEYWORDS
heterogeneous catalyst, heteropolyanion, metal–organic frameworks, methanolysis, MIL-101(Cr)

1 | INTRODUCTION

Metal–organic frameworks (MOFs) are hybrid crystalline porous materials, in which metal ions or clusters are interconnected by organic bridging ligands.[1,2] The combination of organic and inorganic building blocks into highly ordered and crystalline structures provides an almost infinite number of materials with fine-tunable pore size, shape and structure, which also can be used for further grafting, functionalization and encapsulation in the MOF scaffold. Thermal stability of MOFs may exceed 400 °C, and their chemical resistance is good in most cases.[3] Due to their versatility, MOFs have found applications in, for example, gas adsorption and separation[3–5] and sensing,[6] while there are examples of their use as drug carriers[7] and in magnetism.[8,9] One of the key areas of application is as scaffolds to immobilize homogeneous catalysts.[10–14] For the latter application,

MOFs can be functionalized at the organic linker, or catalytic units can be encapsulated into the pore spaces. In this sense, MOFs hold the promise of allowing 'heterogenization' of many homogeneous catalysts with far-reaching consequences in industrial chemistry.

Polyoxometalates (POMs) are anionic metal–oxygen clusters comprised of transition metals such as W, Mo, Nb and V. POMs provide a large and distinct class of molecular inorganic materials that exhibit a broad range of tunable electronic, structural, magnetic,[15,16] redox[17] and catalytic properties.[18–21] Individual properties of POMs lead to many applications, and POMs are favoured as catalysts, especially for 'green' chemistry due to their noncorrosive nature, low amount of waste and high stability.[22] While POMs are large molecules that form clusters of colloidal size range, these are hard to separate from a solution, and hence in their properties POMs are closer to homogeneous catalysts. Moreover 'bulk' POM particles have a low specific surface area (1–5 $m^2 g^{-1}$) that reduces their turnover frequency (TOF) in catalytic applications.[23] Thus, a specific objective of the development of POM catalysis is to acquire stable heterogeneous catalysts with high surface area to associate the high activity of POMs with the superiority of heterogeneous catalysts, such as simple recovery and recycling. To this end, POMs have been adhered to various supports such as silica surfaces,[24–26] titania,[27] active carbon[28,29] and zeolite.[30] These supports, however, have serious limitations such as reduction of activity, low catalyst retention and low capacity for catalyst loading that preclude their successful application. To overcome these limitations, recent developments in this field have focused on encapsulation of POMs within the cavities of MOFs.[31–34]

When materials are larger than the pores of a support material, the impregnation method cannot be used. In this case, there are two strategies for encapsulation in a porous framework: 'build ship in bottle' and 'build bottle around ship'.[13,23] MIL-101(Cr) is a frequently used scaffold material due to its very large pore size and effective surface area with large pore windows.[31,35–40]

In spite of the fact that the direct impregnation of POM species into the large pores of MIL-101(Cr) has been attempted before, there are two main issues associated with this approach: (a) the dispersion of the active species is suboptimal as the large cavities of MIL-101(Cr) are filled with POM and the smaller ones remain vacant; and (b) substantial leaching has been observed as the immobilization is based on the adsorption equilibrium. Thus successful POM encapsulation requires a one-pot 'build bottle around ship' synthesis that has been demonstrated previously.[41]

Epoxides have attracted substantial attention as building blocks in organic synthesis and synthesis intermediates.[42–44] Ring-opening reactions of epoxides to achieve β-substituted alcohols with aromatic and heteroaromatic nucleophiles provide advantageous pathways in organic synthesis. In general, these reactions proceed under either basic or acidic conditions.[45] Several heterogeneous catalysts such as graphite oxide,[46] zirconium-doped mesoporous silica,[47] lanthanide–organic coordination polymer[48] and MOF-based catalysts[49] have been evaluated for alcoholysis of epoxides. Jiang and co-workers have used sulfonic acid-functionalized MIL-101, which also includes both Lewis acidic and Brønsted acidic sites, for alcoholysis of various epoxides.[50] Phosphotungstic acid ($H_3PW_{12}O_{40}$) was encapsulated into MIL-101 by Wee and co-workers.[51] This Lewis acid catalyst has been used for methanolysis of styrene epoxide.

In the work presented here, $K_5[CoW_{12}O_{40}]\cdot 3H_2O$ (Co-POM) was encapsulated into MIL-101, synthesized in the absence of HF, by a one-pot procedure to prepare Co-POM@MIL-101 catalyst. The catalytic activity of Co-POM@MIL-101 was investigated in the ring-opening reaction of epoxides under mild conditions (Scheme 1). High activity, short reaction time, facile recovery and recycling of the catalyst make this new hybrid material highly advantageous for industrial applications.

2 | EXPERIMENTAL

2.1 | Materials and instrumentation

All reagents were purchased at ACS reagent grade from Merck or Fluka. Co-POM was prepared according to the literature.[52] X-ray diffraction (XRD) analysis was conducted with a Bruker D8 Advance instrument using Cu K_α ($\lambda = 1.5406$ Å) radiation. The chemical composition was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES), with a Jarrell-Ash 1100 ICP analyser. Specific surface area, pore volume and pore size were measured by adsorption–desorption of N_2 gas at 77.360 K using a Micrometrics ASAP 2000 instrument. Fourier transform infrared (FT-IR) spectra were obtained in the range 400–4000 cm^{-1} using a JASCO 6300D instrument. Diffuse reflectance spectra were recorded with a JASCO V-670 UV–visible spectrophotometer. The particle size and microscopic morphological features of samples were imaged with a Sigma-Zeiss
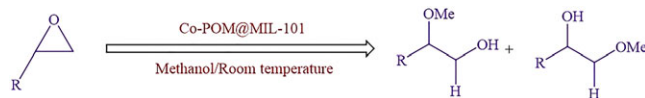
SCHEME 1 Methanolysis of epoxides catalysed by Co-POM@MIL-101

field-emission scanning electron microscopy (SEM) instrument. Transmission electron microscopy (TEM) with an FEI Tecnai-20 microscope was applied to characterize crystal morphology and size of the new catalyst as well as the dispersion of the POM. Finally the progress of the reactions was monitored using GC analysis with an Agilent GC6890 equipped with a 19096C006 80/100 WHP packed column and a flame ionization detector.

2.2 | Synthesis of HF-free MIL-101

MIL-101 samples were synthesized hydrothermally according to a formerly reported method by Bromberg et al.[38] in the absence of HF. In this method, $Cr(NO_3)_3 \cdot 9H_2O$ (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol) and deionized water (20 ml) were mixed, and then the mixture was put in a Teflon-lined hydrothermal synthesis autoclave reactor and kept in an oven at 218 °C for 18 h without stirring. After the synthesis and cooling to room temperature, green raw product was separated by centrifugation and washed with water, methanol and acetone, and then dried and activated overnight under vacuum.

2.3 | Synthesis of co-POM@MIL-101

This composite material was prepared by mixing the MIL-101 precursor and the synthesized Co-POM and water in an autoclave. In a typical procedure, $Cr(NO_3)_3 \cdot 9H_2O$ (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol), Co-POM (in different amounts of 2.0, 1.6, 0.8 and 0.4 g) and deionized water (20 ml) were mixed and sonicated for a short time resulting in a dark blue coloured mixture. The suspension was put in a Teflon-lined hydrothermal synthesis autoclave reactor and kept in an oven at 218 °C for 18 h without stirring. The resulting Co-POM@MIL-101 solid was separated by centrifugation and washed with water, methanol and acetone, and then activated under vacuum until fixed weight.

2.4 | Catalytic reaction

Methanolysis reactions of various epoxides such as styrene oxide, 2-(phenoxymethyl)oxirane and 2-[(allyloxy) methyl]oxirane were performed a 25 ml round-bottomed flask at room temperature to afford the corresponding alcohols in excellent yields in the presence of the Co-POM@MIL-101 heterogeneous catalyst. The required amount of Co-POM@MIL-101 was added to a solution of 1 mmol of epoxide in 5 ml of methanol. The mixture was stirred for 30 min at room temperature. The progress of the reaction was monitored by GC.

2.5 | Catalyst recovery and reuse

In order to investigate the recyclability and reusability of the catalyst, it was filtered from the reaction medium and washed with water, ethanol and acetone. The reusability of the Co-POM@MIL-101 catalyst was investigated repeatedly in methanolysis of styrene epoxide as explained above. The catalyst was recovered from the reaction medium by filtration at the end of each cycle, then washed, activated and reused for four cycles with a negligible catalyst leaching and a slight decrease of its activity. The amount of POM leached after first run in the filtrates was determined using ICP-OES. The structural stability of the catalyst was investigated using XRD. The catalytic activity of this hybrid material was compared with that of previously reported catalytic systems.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of co-POM@MIL-101 catalyst

The XRD patterns of MIL-101 and the synthesized catalyst, Co-POM@MIL-101, are shown in Figure 1. There are similarities between the simulated results presented in previous literature and the pattern of the synthesized MIL-101 which indicates structural confirmation of the MOF.[31,53,54] As shown in Figure 1, the peak intensities of the isostructural catalyst are reduced somewhat compared to pure MIL-101 which can be related to the encapsulated POM, but the crystal structure remains. The Co-POM peaks in the XRD pattern are weak, which can be attributed to the deficiency of large Co-POM crystals on the exterior surface of MIL-101.[55]
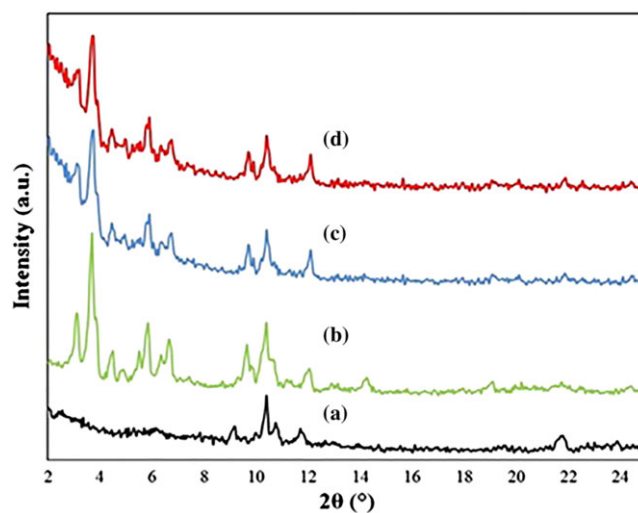
FIGURE 1 XRD patterns of (a) Co-POM, (b) MIL-101, (c) Co-POM@MIL-101 and (d) recovered catalyst after four cycles

TEM and SEM images of the Co-POM@MIL-101 hybrid material are shown in Figure 2. These images reveal micrometre-sized crystallites with sizes and shapes similar to those previously reported.[23,56,57] Spherical interior particles illustrate incorporation of Co-POM into the MOF pores. Also, the energy-dispersive X-ray (EDX) results, obtained from SEM analysis of the catalyst in Figure 3(a), clearly show the presence of Co and W from the POM and Cr related to MIL-101(Cr). Furthermore, the elemental mapping analysis indicates a good distribution of Co-POM into the pores of MIL-101(Cr) (Figure 3b).

Figure 4 shows the UV–visible spectrum of MIL-101 containing Co-POM in comparison with those of bare MIL-101 and Co-POM. The absorption band at 255 nm corresponds to oxygen–tungsten charge transfer assigned to Keggin anions.[23] The d–d charge-transfer transition

FIGURE 2 (a) SEM image and (b) TEM image of Co-POM@MIL-101

of the cobalt cation is observed at *ca* 512 nm. It is noted that d–d charge-transfer transition of cobalt cation in Co-POM is shifted from 512 to 562 nm; this red shift can be ascribed to the strong coordination interaction between the cobalt cation and oxygen atoms in the POM structure.[58] Although the intensities are weaker, these peaks are also observed in the spectrum of Co-POM@MIL-101. Also, the UV–visible spectra provide further evidence of the intact MIL-101 structure. The diffuse reflectance spectrum of the encapsulated POM parallels the spectrum of the free homogeneous POM species.

The intact structure of the POM in the composite material was also confirmed using FT-IR vibrational spectroscopy. As shown in Figure 5(b), the FT-IR spectrum of Co-POM@MIL-101 is the sum of the characteristic bands of the free components: Co-POM (Figure 5a) with characteristic peaks in the region 700–1200 cm^{-1} assigned to W=O, W—O—W and Co—O bonds[59,60] and MIL-101 (Figure 5c) with characteristic vibrational bands of (O—C—O) groups of the framework around 1550 and 1400 cm^{-1} and of C=O vibrations at 1708 and 1658 cm^{-1}.[61]

Nitrogen physisorption analysis (Figure 6) was used to verify the constant porosity of Co-POM@MIL-101. The strong uptake at a low relative pressure in N_2 adsorption–desorption isotherms is the typical characteristic of a microporous material.[51] The quantity of gas absorbed during Brunauer–Emmett–Teller (BET) nitrogen absorption isothermal analysis (Table 1) demonstrated that the pore volume of Co-POM@MIL-101 was three times smaller than that of bare MIL-101 that is consistent with loading of Co-POM into the pores of MIL-101, however still sufficient for reagent diffusion in a catalysis application. The BET surface area shows a predictable decrease from 2730 to 988 $m^2\ g^{-1}$.

3.2 | Catalytic performance

Most of the ring-opening reactions of epoxides under acidic conditions lead to a combination of regioisomers, and polymerization has been observed. One of the reported catalysts for the ring-opening reactions of epoxides by various nucleophiles is a one-electron transfer catalyst.[62–65] We have previously introduced Co-POM as a benign and highly efficient catalyst for alcoholysis of epoxides[66]; here in the Co-POM@MIL-101 catalyst, POMs are the active centres and MIL-101 material is the support, which provides high surface area and mesoporous cages to encapsulate POMs.
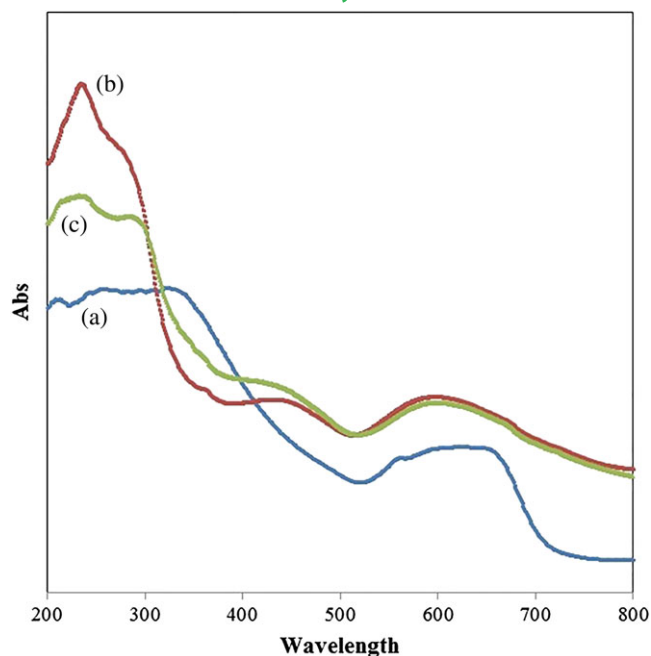
We suggest that selective ring opening of various epoxides with methanol proceeds through an electron transfer mechanism. In previous work we have shown that addition of a small amount of acrylonitrile to the
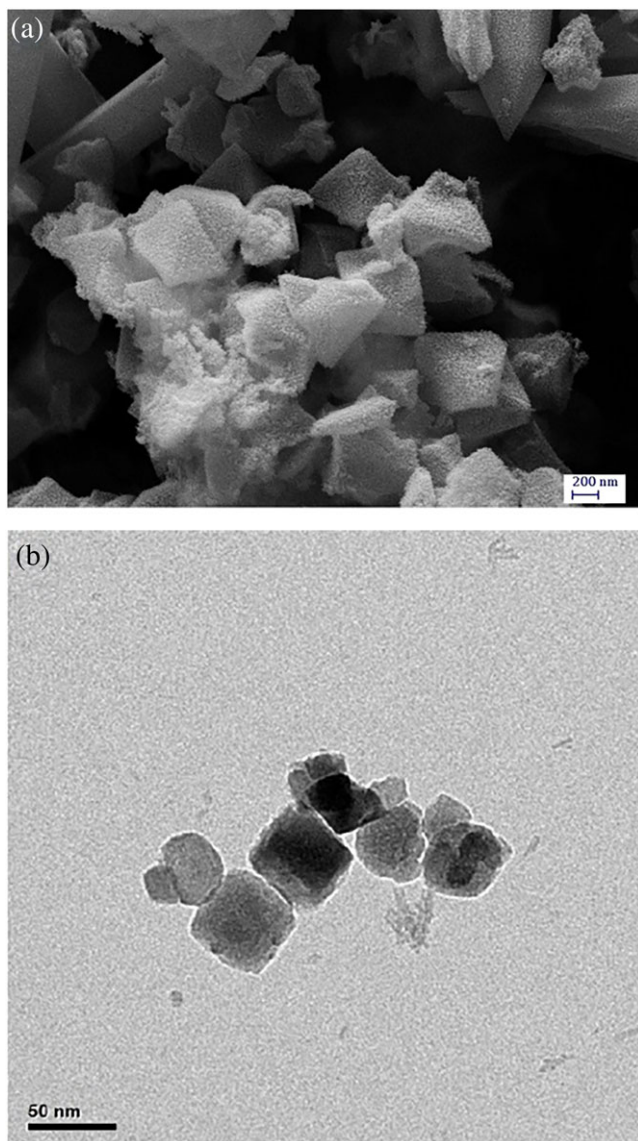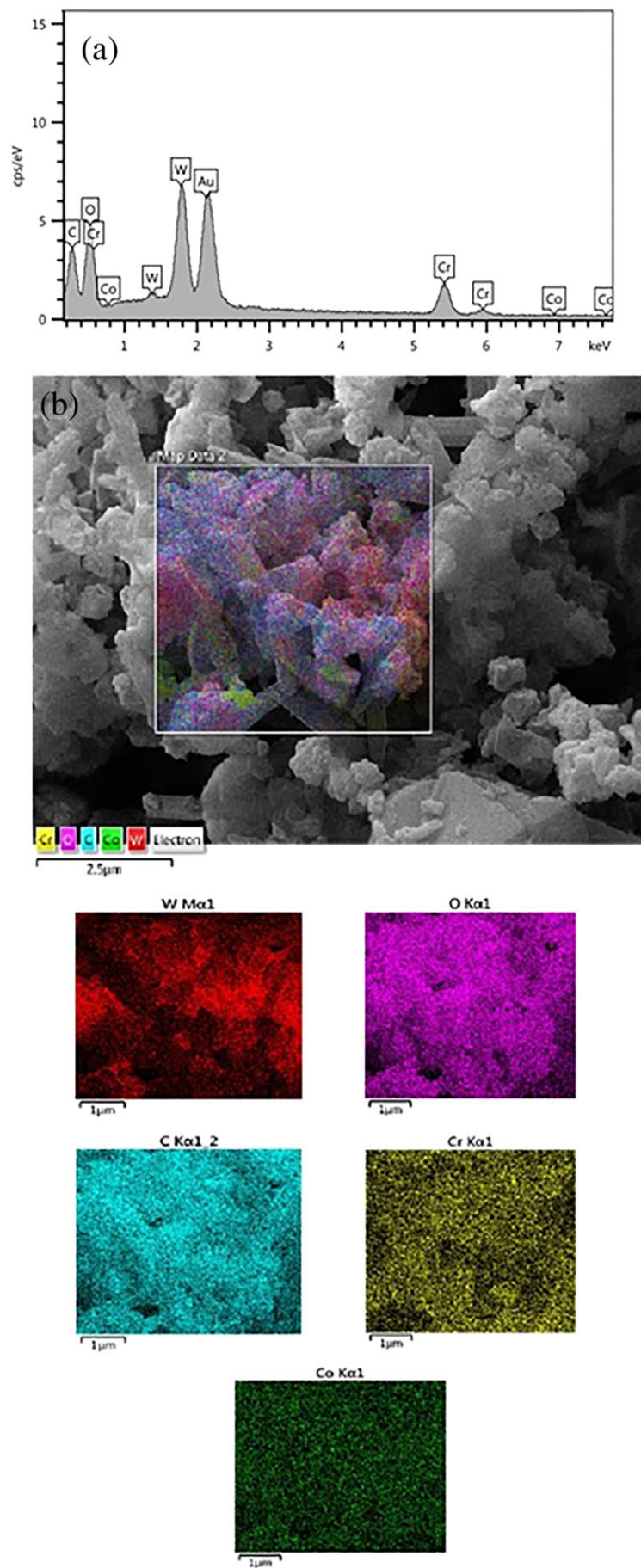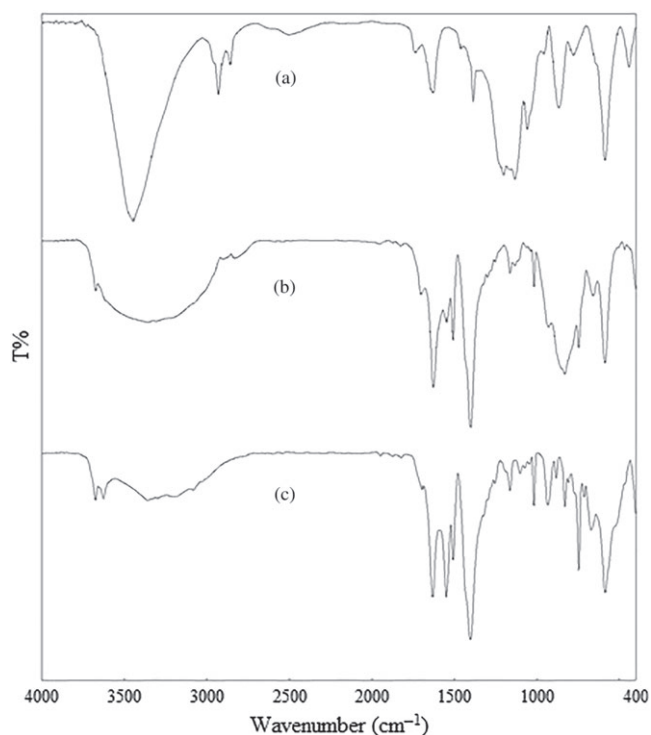
FIGURE 3 (a) SEM-EDX analysis and (b) mapping of the hybrid Co-POM@MIL-101 material (Au is from the sample holder)
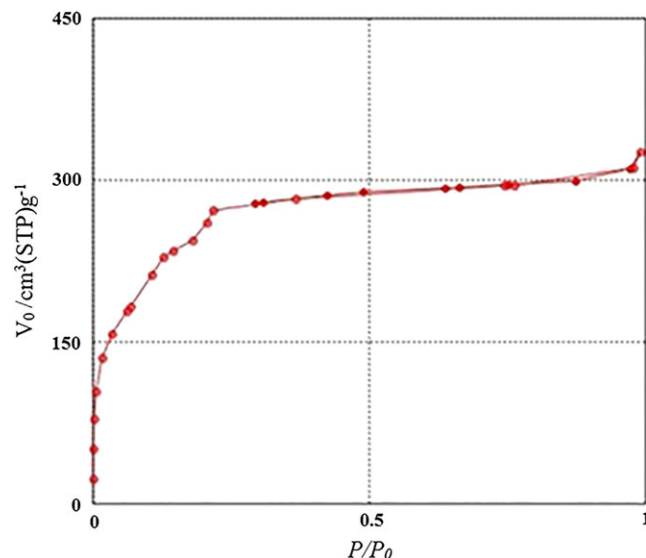
FIGURE 4 UV–visible spectra of (a) Co-POM, (b) MIL-101 and (c) Co-POM@MIL-101

FIGURE 5 FT-IR spectra of (a) Co-POM, (b) Co-POM@MIL-101 and (c) MIL-101

FIGURE 6 N_2 adsorption-desorption isotherm of Co-POM@MIL-101 (open symbols, adsorption; filled symbols, desorption)

reaction mixture as radical scavenger leads to a large decrease in the reaction rates, consistent with an electron transfer mechanism.[66] In previous studies, $[CoW_{12}O_{40}]^{5-}$ was demonstrated to be a well-defined outer-sphere electron-transfer agent in organic chemistry.[67,68] Since in the complex the empty orbitals of cobalt have lost the ability to interact directly with epoxides due to their complete coverage with 12 inactive WO_6 ligands, only outer-sphere electron transfer is possible. First, the electrons are transferred from the oxygen atoms of the epoxides to the inactive WO_6 ligands, and then added to the buried cobalt orbital. The result of this transformation is a cation radical intermediate that is easily attacked by the alcohols leading to epoxide ring opening.

The amount of initial POM during encapsulation in MIL-101 is a crucial factor in this reaction; therefore, the effect of the initial amount of POM was investigated in the synthesis of the catalyst. Co-POM@MIL-101 was synthesized using 0.4, 0.8, 1.6 or 2.0 g of Co-POM, 2.0 g of $CrNO_3$ and 0.83 g of terephthalic acid as initial precursors for the synthesis of MIL-101, and then the catalytic performance of these hybrid materials was evaluated in the methanolysis of styrene epoxide. When Co-POM@MIL-101 with 0.4 g of POM was used, the conversion reached 90% within 30 min; in the case of 0.8 g of POM, the conversion reached 100% in the same time. It is noteworthy that, when using 1.6 and 2.0 g of POM, a significant decrease was observed in the conversion (Table 2). This is believed to be because of the total filling of the pore volume therefore hampering the mass transfer of the reactants to the active species. The catalytic activity of pure MIL-101 was also investigated in the model reaction and, while it was not entirely inactive, only 20% of the desired product was produced. Hence, Co-POM@MIL-101 synthesized with 0.8 g of POM was chosen as the appropriate catalyst. The amount of POM loading was

TABLE 1 Specific surface area and total pore volume of MIL-101 and the prepared catalyst

Sample	BET surface area ($m^2 g^{-1}$)	Average pore diameter (nm)	Total volume ($cm^3 g^{-1}$)
MIL-101	2730	3.6	1.35
Co-POM@MIL-101	988	2.0	0.5

TABLE 2 Effect of initial POM amount on the catalytic activity of co-POM@MIL-101 catalyst in methanolysis of styrene epoxide[a]

Entry	Co-POM (g)	Time (min)	Yield (%)[b]
1	0	30	20
2	0.4	30	90
3	0.8	30	100
4	1.6	30	70
5	2	30	40
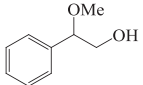
[a]Reaction conditions: epoxide (1 mmol), MeOH (5 ml), catalyst (150 mg), room temperature.

[b]GC yield based on epoxide.

determined using ICP-OES analysis based on the amount of cobalt which showed a value of ca 0.0084 mmol g^{-1}.

The amount of Co-POM@MIL-101 catalyst per volume of reaction mixture was also optimized. As shown in Figure 7, when 50 mg of catalyst was employed, the yield reached 45% with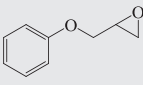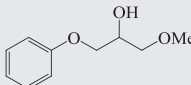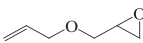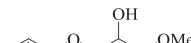in 30 min. As the amount of catalyst increased to 150 mg, the yield reached 100% within 30 min. However, using a greater amount of catalyst, the time required to achieve 100% efficiency did not reduce. Hence, 150 mg was chosen as the optimized amount of catalyst in this reaction. As a negative control, no product was observed in the absence of the catalyst after 30 min.
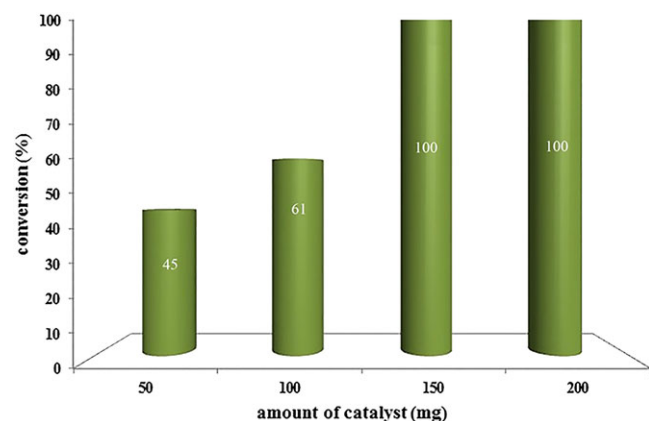
FIGURE 7 Optimization of catalyst amount. Reaction conditions: styrene epoxide (1 mmol), MeOH (5 ml), Co-POM@MIL-101, room temperature
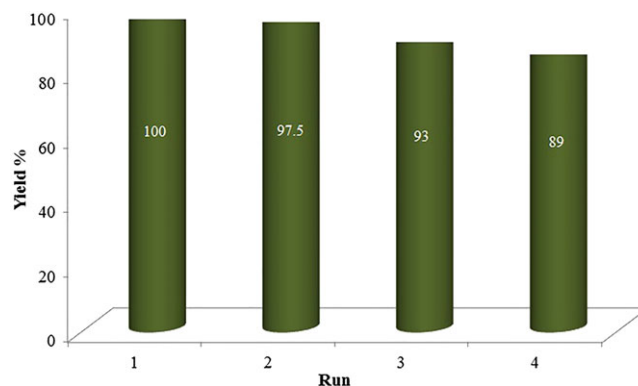
FIGURE 8 Recycling of Co-POM@MIL-101 in the methanolysis of styrene epoxide, reaction conditions: styrene epoxide (1 mmol), MeOH (5 ml), Co-POM@MIL-101 (150 mg), room temperature

TABLE 3 Methanolysis of various epoxides catalysed by co-POM@MIL-101[a]

Entry	Epoxide	Time (min)	Product	Selectivity (%)	Yield (%)[b]	TOF (h^{-1})
1		30		100	100	1504
2		30		100	96	1443
3		30		100	88	1323

[a]Reaction conditions: epoxide (1 mmol), MeOH (5 ml), catalyst (150 mg), room temperature.

[b]GC yield based on epoxide.

TABLE 4 Comparison of catalytic performance of co-POM@MIL-101 and reported MOF-based catalysts for methanolysis of styrene oxide

Entry	Catalyst	Temperature (°C)	Time (min)	Yield (%)	Reusability (runs)	TOF (h^{-1})	Ref.
1	MIL-101-SO$_3$H	RT	30	99	5	99	[50]
2	MIL-101(HPW)	40	20	99.8	3	98.5	[51]
3	Cu-MOF	RT	120	93	4	5.3	[69]
4	HKUST-1	40	150	90	No data	5.6	[70]
5	[Fe (BTC)]	40	60	93	3	9.3	[49]
6	Co-POM@MIL-101	RT	30	100	4	1504	Present work

Under the optimized reaction conditions, allyl glycidyl ether and phenyl glycidyl ether were subjected to methanolysis in the presence of Co-POM@MIL-101. The results show that these two linear epoxides were successfully converted to their corresponding β-methoxy alcohols in excellent yields (Table 3). While the TOF for homogeneous catalyst, Co-POM, was about 80 h^{-1},[66] the TOF reached *ca* 1500 h^{-1} for Co-POM@MIL-101. The singular catalytic activity of the heterogeneous catalyst can be ascribed to trapping of the catalytic active sites (Co-POM) within the MOF pores.

3.3 | Catalyst reuse and stability

One of the important factors for a solid catalyst system is the stability of the active component under reaction process with regard to maintaining structural integrity and leaching of the catalyst. To study the stability and reusability of the active Co-POM component in the Co-POM@MIL-101 catalyst, a four-cycle series of experiments was performed using methanolysis of styrene epoxide as a model reaction (Figure 8). To prevent the reduction of catalyst performance, the catalyst was washed with water, ethanol and acetone to remove trapped reactants after each cycle and activated under vacuum at 100 °C overnight. The amount of Co-POM remaining in the catalyst was determined using ICP-OES analysis. Approximately 0.01 wt% Co-POM leached from the catalyst after one run. The XRD pattern of the Co-POM@MIL-101 catalyst after four cycles of the methanolysis of styrene epoxide still showed the characteristic peaks of Co-POM@MIL-101 (Figure 1d). Thus the structural integrity of Co-POM@MIL-101 is maintained during the four reaction cycles.

In order to investigate the nature of the catalyst (homogeneous versus heterogeneous) in the studied reaction, two paths were followed. In the first one, solid catalyst was removed from the reaction media after 10 min of reaction and reaction progress was followed by GC. No further conversion was observed. In the other pathway, one of the reactants (methanol) and the

activated catalyst were stirred under reaction conditions for 1 h; then the catalyst was separated by filtration and the other reactant (epoxide) was added to the reaction vessel and the reaction mixture was stirred again. No noticeable conversion was obtained in the reaction when following this sequence which confirms the heterogeneous nature of the catalyst.

For demonstration of the efficiency of the present catalyst and to complete our work, the catalytic performance of this catalyst was compared with that of some MOF-based catalysts reported previously in the literature. The results, which are summarized in Table 4, show that this catalyst is preferable in respect of reaction temperature and conversion time and mostly in TOF.

4 | CONCLUSIONS

We report the successful synthesis of a new hybrid catalyst by encapsulation of Co-POM into MIL-101 synthesized in a one-pot process. The catalytic activity of this heterogeneous catalyst was investigated in the methanolysis of epoxides. The results indicated that the TOF value of Co-POM@MIL-101 was more than 20 times higher than that of homogeneous Co-POM catalyst. Easy preparation, reusability and incredibly benign reaction conditions are other important factors that make Co-POM@MIL-101 an efficient and unique immobilized catalyst.

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