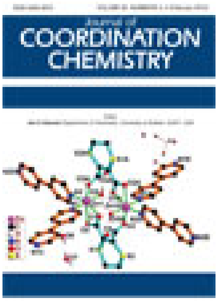

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The effect of encapsulated Zn-POM on the catalytic activity of MIL-101 in the oxidation of alkenes with hydrogen peroxide

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Zinc monosubstituted Keggin heteropolyanion $[PZnMo_2W_9O_{39}]^{5-}$ was electrostatically bound to nanocages of MIL-101 polymer matrix. The Zn-POM@MIL-101 catalyst was characterized by XRD, N_2 adsorption, atomic absorption (AAS), and FT-IR spectroscopic methods. The catalytic activity of the new composite material, Zn-POM@MIL-101, was assessed in the oxidation of alkenes using aqueous hydrogen peroxide as oxidant. Zn-POM@MIL-101/H_2O_2 catalytic system demonstrated good catalytic activity in the oxidation reactions. Zn-POM@MIL-101 was reusable for three catalytic cycles. While the MIL-101 matrix is an active catalyst in these oxidation reactions, the presence of Zn-POM significantly changed the selectivity and reaction times.

Keywords: Metal–organic framework; MIL-101; Supported polyoxometalate; Alkene oxidation; Hydrogen peroxide; Nanoporous material

1. Introduction

Polyoxometalates (POMs), as a unique class of metal-oxide clusters [1–5], have many properties that make them candidates for application in catalysis, medicine, and materials science [6, 7]. Due to their advantageous properties such as inorganic nature, thermodynamic stability toward oxidation, hydrostability, tunability of redox and acid properties, etc. [8–10], the preparation of POM-based materials is still a vibrant field of study [11]. For instance, polyoxometalates are applied as homogeneous catalysts in oxidation reactions with hydrogen peroxide. Catalytic oxidations with hydrogen peroxide have the following advantages: (i) water is the sole by-product, (ii) it has a high content of active oxygen species, and (iii) it is much cheaper and safer to use than organic peroxides or peracids [12].

Although many efficient oxidation systems with hydrogen peroxide in the presence of POMs have been developed, most of them are homogeneous and have general disadvantages such as difficult catalyst/product separation, poor catalyst reusability, and recoverability [13–16]. Hence, practical application of POMs in the oxidation

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reactions requires the development of easily recoverable and recyclable catalysts. One approach in this area is the heterogenization of catalytically active species [12].

Metal–organic frameworks (MOFs) have attracted attention because of their unique combination of properties such as high surface area, crystalline open structures, tunable pore size, and functionality [17–21]. These properties allow MOFs as prospective catalytic materials and supports for immobilization of homogeneous catalysts [22–29].

Recently, new methods based on MOFs such as: (i) catalysis by homogeneous catalysts incorporated as framework struts [30, 31], (ii) catalysis by MOF-encapsulated molecular species [32], and (iii) catalysis by MOF-encapsulated clusters [10, 33–36] have been reported for heterogenization of active homogeneous catalysts.

MIL-101 possesses a rigid zeotype crystal structure, extremely large surface area and quasi-spherical cages of two types (free internal diameters are close to 29 and 34 Å, while the cages are accessible through microporous windows of about 12 and 16 Å). MIL-101 is resistant to air, water, common solvents, and thermal treatment (up to 320°C) [18, 37]. Transition metal monosubstituted POMs (M-POMs) are valuable single-site catalysts where active metal, M, is isolated and strongly bound to an inorganic metal–oxide matrix and thus is prevented from oligomerization and leaching [38, 39].

Therefore, MIL-101 supported polyoxometalates have attracted considerable attention [10, 33–36]. In this study, we report the preparation of a heterogeneous catalyst, based on nanoporous MIL-101 metal organic framework, and catalytically active Zn-monosubstituted Keggin type heteropolyanions, $[(n\text{-Bu})_4N]_5PZnMo_2W_9O_{39}\cdot 3H_2O$, which has been incorporated within the coordination polymer nanocages. The catalytic performance of this catalyst was investigated in the oxidation of alkenes with hydrogen peroxide.

2. Experimental

2.1. *General*

All reagents were obtained commercially and used without purification. Hydrogen peroxide was used as 30% solution in water. The *tetra-n*-butyl ammonium salt of monosubstituted POM $[PZnMo_2W_9O_{39}]^{5-}$ was prepared from $\alpha\text{-}K_7PMo_2W_9O_{39}$ by a slight modification of the previously reported method [40].

FT-IR spectra were recorded using potassium bromide pellets from 400 to 4000 cm^{-1} by a Jasco FT/IR-6300 instrument. GC analyses were performed using a Shimadzu GC-16A gas chromatograph equipped with a flame ionization detector and a 2 m column packed with silicon DC-200 or Carbowax 20 M. The products were identified by comparing their retention times with known samples. Powder X-ray diffraction patterns were obtained on a D_8 Avance Bruker using Cu Kα ($\lambda = 1.5406$ Å). Mass analyses were performed using a Micromass platform 8379E spectrometer. ^1H NMR spectra were recorded by a Bruker 400 MHz instrument using $CDCl_3$ as solvent. Thermogravimetric analyses (TGA) were performed on a Mettler TA 4000 instrument at a heating rate of 10 $K \cdot min^{-1}$. The accelerated surface area and porosimetry (ASAP) analyses were carried out at low temperature by adsorption of N_2 gas with an ASAP 2000 micromeritics instrument.

2.2. *Preparation of catalyst*

2.2.1. MIL-101 synthesis. The coordination polymer MIL-101 was prepared as described by Férey *et al.* [37]. In a typical procedure, a mixture of $Cr(NO_3)_3{\cdot}9H_2O$ (1.2 g, 3 mmol), terephthalic acid (H_2bdc, 500 mg, 3 mmol), and HF (0.6 mL of $5\,mol\,L^{-1}$, 3 mmol) in H_2O (15 mL) was heated at 220°C for 8 h in a Teflon-lined stainless steel autoclave. The resultant green solid was passed through a coarse filter to eliminate unreacted crystals of H_2bdc and then filtered on a thick filter. Then the green raw product was washed two times with hot DMF for 8 h (100°C) and twice with hot EtOH for 8 h (80°C), filtered off, and dried overnight in an oven at 75°C.

2.2.2. Immobilization of Zn-POM on MIL-101. Zn-POM@MIL-101 catalyst was prepared as follows: $[(n\text{-Bu})_4N]_5PZnMo_2W_9O_{39}{\cdot}3H_2O$ (22 mg) was dissolved in CH_3CN (2 mL) and MIL-101 (100 mg) was added to this solution and stirred for 6 h. The resulting solid was stored overnight at room temperature and then filtered off. The solids were washed with CH_3CN and dried under air until the weight remained constant. The complete disappearance of Zn-POM in the CH_3CN solution was established by UV-Vis spectroscopy. The Zn-POM loading was also evaluated by atomic absorption spectroscopy (AAS). The catalyst was characterized by XRD, TG/DTG, FT-IR spectroscopy, and adsorption–desorbtion of N_2 gas.

2.3. *General procedure for oxidation of alkenes*

In a 25 ml round-bottom flask equipped with a magnetic stir bar and a condenser, the catalytic experiments were carried out under reflux (70°C). The H_2O_2 (5 mmol) was added to a mixture of alkene (0.5 mmol) and catalyst (5 mg, 2.3×10^{-4} mmol Zn-POM) in acetonitrile (3 mL). The reaction progress was monitored by GC. At the end of the reaction, the catalyst was filtered and washed with acetonitrile (10 mL). The filtrates were concentrated and purified on a short column of silica gel to obtain the pure product. The corresponding carboxylic acids were characterized by FT-IR, ^{1}H NMR spectroscopic methods, and mass spectrometry (Supplementary material).

3. Results and discussion

3.1. *Characterization of catalyst*

MIL-101 was prepared by hydrothermal method as described by Férey *et al.* [37]. The matrix was characterized by X-ray diffraction, FT-IR spectroscopy, and N_2 adsorption–desorption techniques. Figures 1(a) and 2(a) show the XRD pattern and FT-IR spectrum of MIL-101 which is similar to the previously reported ones [10, 37]. Figure 3 shows the schematic representation of Zn-POM encapsulated in the MIL-101 matrix. This catalyst, Zn-POM@MIL-101, was prepared by encapsulation of Zn-POM in acetonitrile solution at 25°C. Similar methods were reported for encapsulation of POM within the MIL-101 pores by Férey and Maksimchuk [10, 37]. Comparison of XRD pattern of Zn-POM@MIL-101 (figure 1b) with the original MIL-101 (figure 1a)

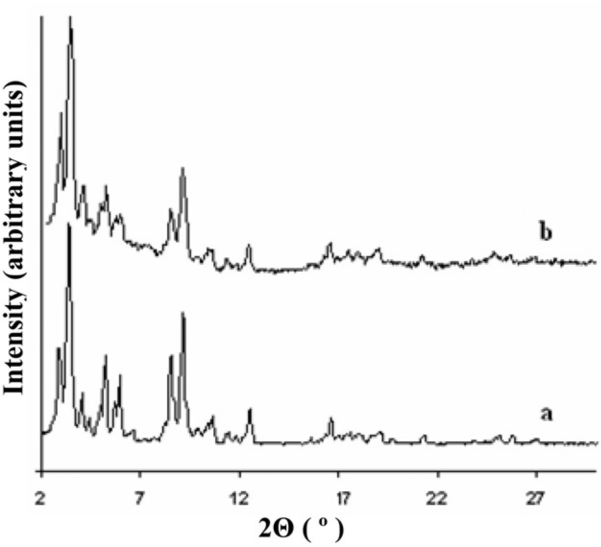

Figure 1. XRD patterns of (a) MIL-101, (b) Zn-POM@MIL-101.

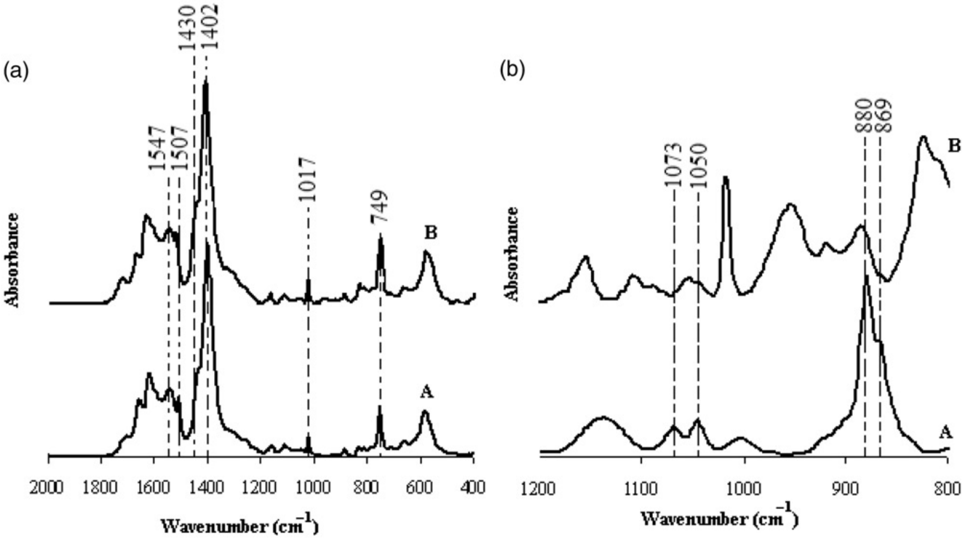

Figure 2. FT-IR spectra of (a) MIL-101 (A) and Zn-POM@MIL-101 (B), (b) Zn-POM (A) and Zn-POM@MIL-101 after subtraction of the spectrum of MIL-101 (B).

shows that the MIL-101 matrix retains crystallinity upon encapsulation of Zn-POM. This similarity indicates strong interaction of POM anion with MIL-101, therefore, the positions of the X-ray reflections, compared to the initial MIL-101 sample, remained unchanged. The interaction between POM anion and the positively charged interior

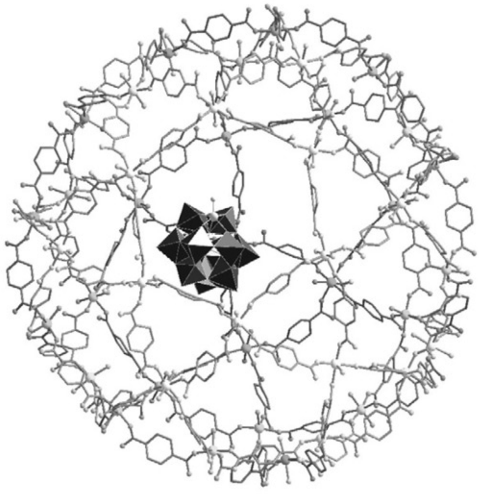

Figure 3. Schematic representation of Zn-POM encapsulated within MIL-101 matrix.

Table 1. Physico-chemical properties of the catalyst studied.

Sample	Zn/Mo/W/Cr[a]	A ($m^2\ g^{-1}$)[b]	V_p ($cm^3\ g^{-1}$)[c]
MIL-101	–	2125	1.08
Zn-POM	1.7/5/43/–		
Zn-POM@MIL-101	0.3/0.87/7.57/17.9	1913	0.98

[a] Evaluated from the atomic absorption data.
[b] Specific surface area.
[c] Mesopore volume.

surface of the MIL-101 nanocages is an electrostatic interaction [36]:

$$n/0.2[Cr_3O(bdc)_3(H_2O)_2F_{0.8}(NO_3)_{0.2}] + POM^{n-}$$
$$\rightarrow [Cr_3O(bdc)_3(H_2O)_2F_{0.8}]_{n/0.2}POM + nNO_3^{-}$$

The FT-IR spectra of MIL-101 and Zn-POM@MIL-101 are shown in figure 2(a). These spectra are similar and the high intensity peaks corresponding to MIL-101 solid matrix. Strong bands at 1300–1800 cm^{-1} belong to ν_{as}(COO), ν_s(COO), and ν(C–C) vibrations from the dicarboxylate linker in the MIL-101 framework. Narrow and weak bands at 1017 and 749 cm^{-1} can be attributed to δ(C–H) and γ(C–H) vibrations of aromatic rings, respectively.

Figure 2(b) shows IR spectra of Zn-POM and Zn-POM@MIL-101 after subtraction of the MIL-101 spectrum. The IR spectrum of Zn-POM@MIL-101 exhibits the principal stretching modes of the Keggin POM unit: 1050 $\nu_{as}(PO_4)$ and 880 cm^{-1} ν_{as}(W–O–W), for Zn-POM. These show that the heteropolyanion structure was sustained after immobilization.

Table 1 shows the physico-chemical characteristics for MIL-101 and Zn-POM@MIL-101. The loading of the catalyst was determined by elemental analysis, indicating that the amount of Zn-POM encapsulated in MIL-101 is 17.5%.

Table 2. Alkene oxidation with H_2O_2 in the presence of MIL-101 and Zn-POM@MIL-101.

		MIL-101[a]			Zn-POM@MIL-101[b]			
Substrate	Acid	Conversion (%)	Time (h)	TOF[c] (h^{-1})	Conversion (%)	Time (h)	Acid yield (%)	TOF[c] (h^{-1})
Cyclopentene	Glutaric acid	75	8	7.10	100	3	98	723
Cyclohexene	Adipic acid	90	8	8.52	95	4	70	516
Cyclooctene	Suberic acid	98	4	18.56	100	4	23	542
Indene	Homophthalic acid	100	3	25.25	94	3	62	680
1-Octene	Heptanoic acid	90	8	8.52	85	4	15	462
1-Decene	Nonanoic acid	80	8	7.57	84	4	12	456
1-Dodecene	Undecanoic acid	85	5	12.88	72	4	7	391

[a] 0.5 mmol alkene, 5 mmol H_2O_2, 5 mg MIL-101(66×10^{-4} mmol), 3 mL CH_3CN, reflux (70°C).
[b] 0.5 mmol alkene, 5 mmol H_2O_2, 5 mg Zn-POM@MIL-101(2.3×10^{-4} mmol ($[(n\text{-Bu})_4N]_5PZnMo_2W_9O_{39}\cdot 3H_2O$)), 3 mL CH_3CN, reflux (70°C).
[c] Turn over frequency.

The specific surface areas and mesopore volumes of MIL-101 and Zn-POM@MIL-101, obtained from the low temperature N_2 adsorption measurements, are shown in table 1 and figure S1 (Supplementary material). The pore volume and specific surface area of MIL-101 decreased upon encapsulation of Zn-POM. Subsequently, in order to investigate the influence of Zn-POM on the thermal stability of MIL-101 matrix, the TG/DTG analysis was also performed. Thermograms are shown in figure S2. Comparison of these thermograms indicated that Zn-POM increases the thermal stability of MIL-101. Below 350°C, the MIL-101 showed about 11% weight loss in three steps, but Zn-POM@MIL-101 composite showed 6.2% weight loss in two steps. At temperatures above 350°C, both materials decomposed.

3.2. *Catalytic oxidations*

The catalytic performance of Zn-POM@MIL-101 was first assessed in cyclooctene oxidation with aqueous H_2O_2 in acetonitrile. To achieve the highest catalytic performance, parameters such as the type of solvent, amount of catalyst and oxidant were optimized in the oxidation of cyclooctene. Acetonitrile, H_2O_2 (5 mmol), and Zn-POM@MIL-101 (5 mg, 2.3×10^{-4} mmol Zn-POM) were chosen as optimal reaction conditions. All reactions were carried out under these conditions and continued until no further progress were observed. The results are shown in table 2. In the absence of catalyst, the conversion was less than 30% and only 1,2-cyclooctanediol was produced. In the case of cyclopentene (table 2, entry 1, figure 4) after 3 h, the conversion was 100% and the amount of glutaric acid was 98%. In the case of cyclohexene and indene (table 2, entries 2 and 4), the conversions were 95% and 94% after 4 and 3 h, respectively. In the oxidation of cyclohexene, adipic acid (70%) was produced as major product and 1,2-cyclohexandiol and allylic oxidation products (enone and enol) were also observed as minor products (figure 4). For indene, homophthalic acid was produced in 62% and allylic oxidation products were also obtained (figure 4). Cyclooctene (table 2, entry 3) was completely oxidized after 4 h. In this case, the main

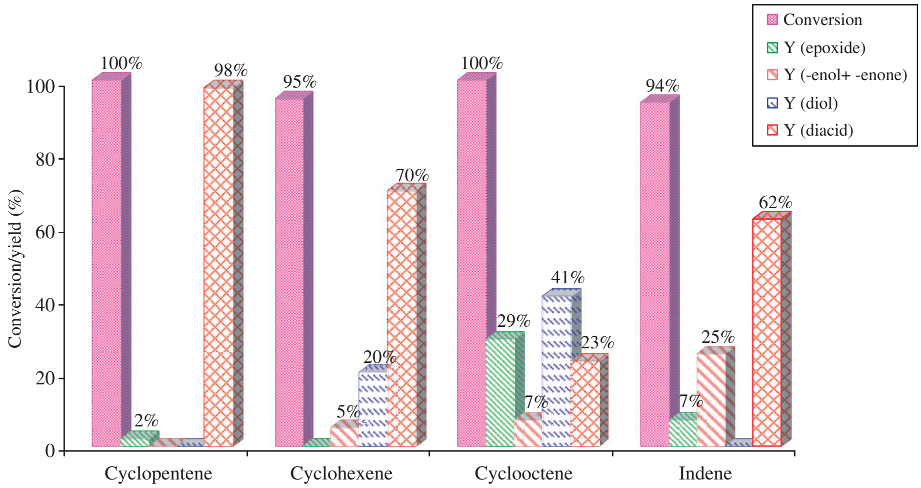

Figure 4. Oxidation of cyclic alkenes with Zn-POM@MIL-101.

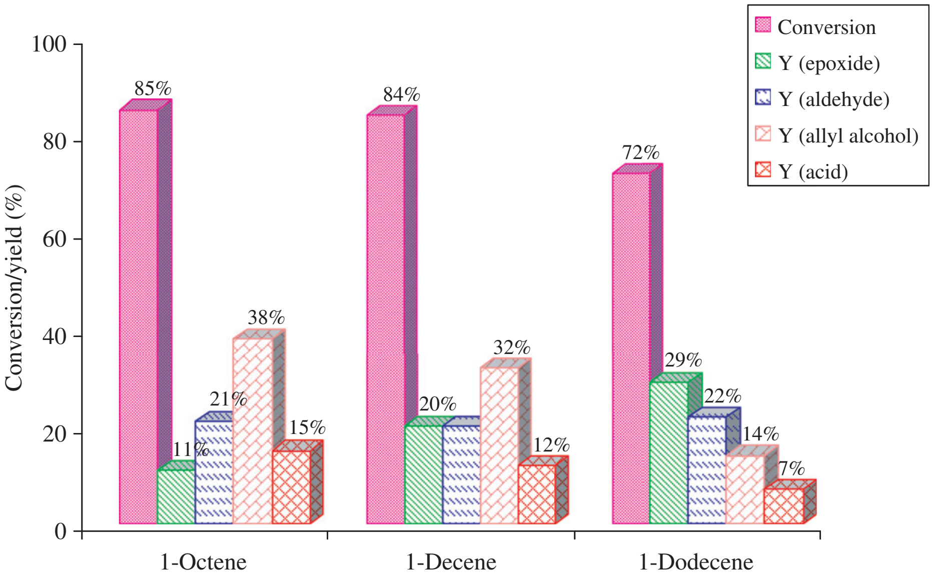

Figure 5. Oxidation of linear alkenes with Zn-POM@MIL-101.

product was 1,2-cyclooctandiol, and epoxycyclooctane and suberic acid were produced in 29% and 23% yields, respectively (figure 4).

For more comprehensive study, oxidations of linear alkenes in the presence of this new composite (Zn-POM@MIL-101) were also performed. The results are shown in table 2 (entries 5–7) and figure 5. In the oxidation of 1-octene, the conversion was 85% after 4 h. In this case, allylic alcohol and aldehyde were produced in 38% and 21% yields (figure 5); other oxidation products like 1,2-epoxyoctane and heptanoic acid were observed. For 1-decene and 1-dodecene, the acid production was decreased while the yield of epoxides increased (figure 5).

Table 3. Reusability of Zn-POM@MIL-101 in the oxidation of cyclooctene with H_2O_2.[a]

Run	Conversion (%)	Epoxide yield (%)	Enone+enol yield (%)	1,2-Cyclooctandiol yield (%)	Suberic acid yield (%)
1	100	29	7	41	23
2	100	34	7	44	15
3	94	56	14	24	0

[a] Reaction condition: 0.5 mmol cyclooctene, 5 mmol H_2O_2, 5 mg Zn-POM@MIL-101 (2.3×10^{-4} mmol $[(n\text{-Bu})_4N]_5PZnMo_2W_9O_{39} \cdot 3H_2O$), 3 mL CH_3CN, reflux (70°C).

In an attempt to show the effect of incorporated Zn-POM on the activity of MIL-101, the reaction of cyclooctene was carried out in the presence of homogeneous Zn-POM (2.3×10^{-4} mmol). The results showed that only epoxycyclooctane was produced in 85% yield after 8 h, and no by-product was detected in the reaction mixture. When the reactions were carried out in the presence of pure MIL-101, the major products were carboxylic acids. On the basis of these observations, in the presence of Zn-POM@MIL-101 the reaction selectivity changed. Therefore, upon incorporating Zn-POM into MIL-101, a new composite was synthesized that show different catalytic activity than MIL-101 and Zn-POM.

3.3. *Catalyst stability and recycling*

Important properties of heterogeneous catalysts are the stability of the active site toward leaching and other transformations and the possibility of catalyst reuse. Therefore, the stability of Zn-POM@MIL-101 was studied in multiple oxidations of cyclooctene with H_2O_2. The catalyst was separated from the reaction mixture after each experiment by sedimentation, washed with the solvent (CH_3CN), and dried carefully before using it in the subsequent run. Indeed, Zn-POM@MIL-101 is recyclable under the reaction conditions for 3 cycles (table 3, figure 6). The results showed that selectivity of reaction considerably changed in the consequent runs. In the first run, 1,2-cyclooctandiol was produced in 41% yield. While in the third run, epoxycyclooctane was detected as a major product. This can be attributed to destruction of the catalyst structure, in which the Zn-POM is leached to the reaction mixture and acts as a homogeneous catalyst. This finding is in accord to results with pure Zn-POM. The FT-IR-spectra (figure 7) showed the destruction of the MIL-101 structure after 3 catalytic cycles, with the appearance of new bands corresponding to stretching C=O vibrations at 1721 and 1686 cm^{-1} along with new stretching OH vibrations at 2940 cm^{-1}, presumably indicating that COO-groups were protonated. These bands can be assigned to the production of terephthalic acid during the catalyst destruction.

The results on using different kinds of POMs in the oxidation of cyclooctene are summarized in table 4. Using different POMs@MIL-101 with a 1/2 molar ratio of cyclooctene/H_2O_2, the epoxide selectivity is 100%. When the molar ratio of cyclooctene/H_2O_2 decreased to 1/10 (by increasing the amount of H_2O_2), the epoxide selectivity decreased significantly. In the presence of homogeneous Zn-POM, both cyclooctene/H_2O_2 ratios gave epoxide as sole product.

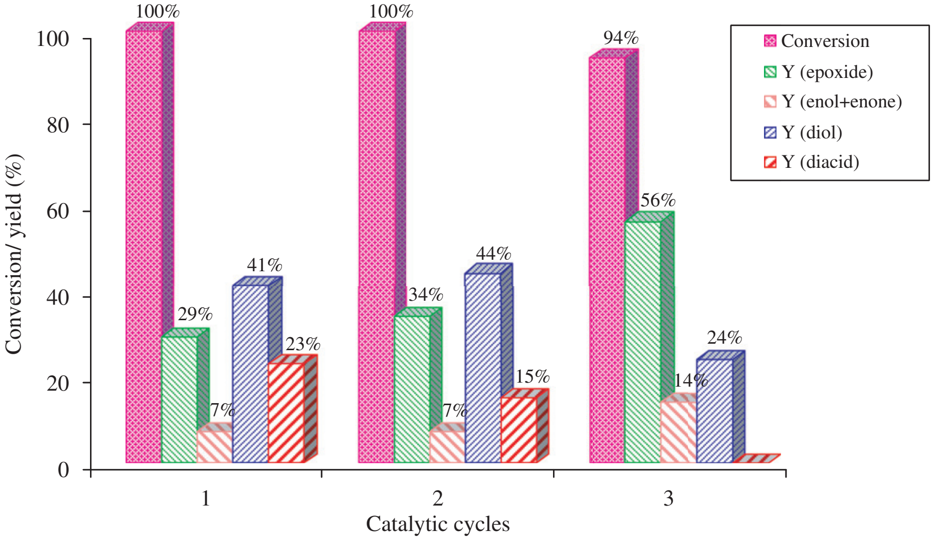

Figure 6. Reusability of Zn-POM@MIL-101 in the oxidation of cyclooctene.

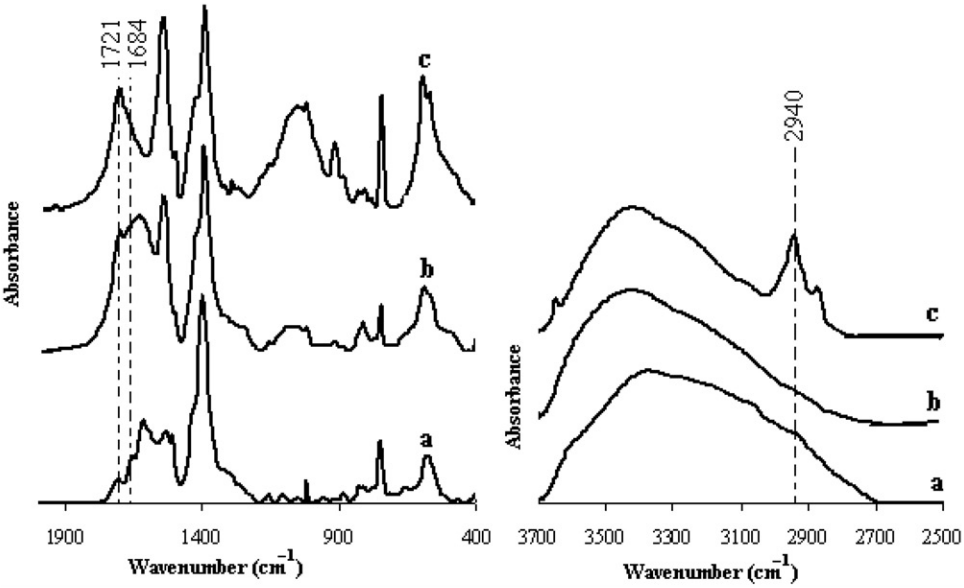

Figure 7. FT-IR spectra of ZnPOM@MIL-101: (a) initial, (b) after first cycle and (c) after three cycles of cyclooctene oxidation with H_2O_2.

4. Conclusions

The findings in this study demonstrated that Zn-monosubstituted Keggin POM can be incorporated electrostatically to nanoporous MIL-101 coordination polymer. The composite Zn-POM@MIL-101 showed catalytic activity in alkene oxidation with H_2O_2 with changed selectivity and reaction times.

Table 4. Results obtained in the oxidation of cyclooctene with H_2O_2 in the presence of different POMs@MIL-101.

Catalyst	Substrate/H_2O_2	T (°C)	Time (h)	Conversion (%)	Epoxide selectivity (%)	Ref.
PW_{12}@MIL-101[a]	1/2	50	3	76	99	[33]
Zn-POM@MIL-101[b]	1/10	70	4	100	29	–
Zn-POM@MIL-101[c]	1/2	70	8	86	100	–
V-POM@MIL-101[d]	1/10	70	4	84	25	–
V-POM@MIL-101[e]	1/2	70	3	32	100	–
Zn-POM[f]	1/10	70	8	85	100	–
Zn-POM[g]	1/2	70	8	81	100	–

[a] 28 mg catalyst (5.8×10^{-3} mmol W, $H_3PW_{12}O_{40}$).
[b] 5 mg catalyst (2.3×10^{-4} mmol Zn, $[(n\text{-Bu})_4N]_5PZnMo_2W_9O_{39}\cdot 3H_2O$).
[c] 7 mg catalyst (3.2×10^{-4} mmol Zn).
[d] 7 mg catalyst (9.3×10^{-4} mmol V, $Na_5[PMo_{10}V_2O_{40}]\cdot 14H_2O$).
[e] 3 mg catalyst (4×10^{-4} mmol V).
[f] 0.88 mg homogeneous catalyst (2.3×10^{-4} mmol Zn).
[g] 1.2 mg homogeneous catalyst (3.2×10^{-4} mmol Zn).

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