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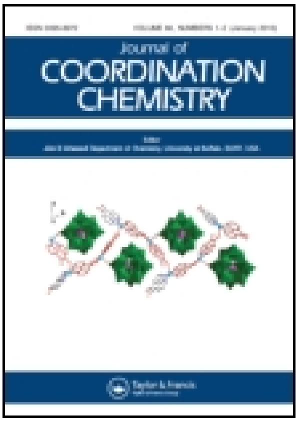

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Olefin epoxidation with tert-BuOOH catalyzed by vanadium polyoxometalate immobilized on ionic liquid-modified MCM-41

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Olefin epoxidation with *tert*-BuOOH catalyzed by vanadium polyoxometalate immobilized on ionic liquid-modified MCM-41

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Preparation and characterization of vanadium-containing polyphosphomolybdates supported on ionic liquid-modified MCM-41, MCM-41-Im, are reported. The catalyst, [PVMo@MCM-41-Im], was characterized by elemental analysis, X-ray diffraction, scanning electron microscopy and also FT-IR, and UV-Vis spectroscopic methods. This heterogeneous catalytic system was applied for efficient epoxidation of various olefins in the presence of *tert*-BuOOH in 1,2-dichloroethane under reflux. The catalyst can be reused several times without apparent loss of its catalytic performance.

Keywords: Immobilized ionic liquid; *tert*-BuOOH; MCM-41; Epoxidation; Polyoxometalate; Heterogeneous catalyst

1. Introduction

Olefin epoxidation is an important reaction for the production of epoxides, a major industrial organic intermediate and is used in the synthesis of drugs, agrochemicals and food additives [1–3].

Due to the unique properties of polyoxometalates (POMs), their syntheses have become an important area of research [4–8]. The catalytic function of POMs has attracted great attention [9–11], due to their hydrolytic and thermal stability, solubility in various solvents and tunable acid and redox properties at the molecular or atomic levels [12–16]. Although the efficiency of homogeneous catalysts is rather high, they suffer from drawbacks such as the non-reusability of the catalyst, degradation, tedious work up for separation of catalyst from products and reactants and decrease in stability toward air, moisture, and temperature. The best way to overcome these problems is immobilization on solid support without loss of their intrinsic activity. Organic and inorganic materials have been used as supports for immobilization of POMs [17–23]. However, inorganic supports exhibit some advantages over organic supports due to higher surface area and chemical stability. A new class of supports in heterogeneous catalysis is MCM-type

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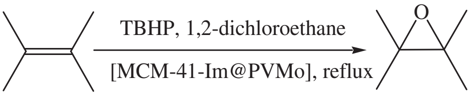


Scheme 1. Olefin epoxidation with TBHP catalyzed by vanadium polyoxometalate immobilized on ionic liquid-modified MCM-41.

mesoporous materials as appropriate host matrices for finely dispersion of POMs within regular pores and channels [24–30]. Large surface areas, hydrophobicity and acidity of these materials can effectively improve their catalytic activity.

Ionic liquids are thermally stable, odorless, and unaffected by moisture. They have no detectable vapor pressure and are immiscible with organic and inorganic solvents. Due to these excellent properties, these materials are used as reaction media for a broad range of catalytic applications [31]. Supported ionic liquid catalysis is a concept that combines the advantages of ionic liquids with those of heterogeneous catalysts [32]. Ionic liquid-modified supported catalysts provide a hydrophobic environment for organic reactions [33–35]. The simple separation and high reusability of these systems make them potentially environmentally benign catalysts in organic reactions.

In this article, the preparation and characterization of vanadium-containing polyphosphomolybdates supported on ionic liquid-modified MCM-41 and its catalytic activity in olefin epoxidation with *tert*-butyl hydroperoxide (TBHP) is reported (scheme 1).

2. Experimental

All chemicals were commercial reagent grade and obtained from Merck and Fluka. Polyoxometalate was prepared according to the literature [36]. The MCM-41 was prepared according to the method reported by Beck *et al.* [37]. The prepared catalyst was characterized by elemental analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), FT-IR, and UV-Vis spectroscopic methods [38]. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with a Jasco Impact 6300D spectrometer. SEM of the catalyst and support were taken on a SEM Philips XL 20 instrument. UV-Vis spectra were obtained from 200 to 800 cm^{-1} with a Jasco V-670 spectrometer. Powder X-ray diffraction patterns were obtained on a D_8 Advanced Bruker using Cu-Kα radiation ($2\theta = 5$–60°). Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. In GC experiments, *n*-decane was used as internal standard. ^{1}H NMR spectra were recorded on a Bruker-Avance AQS 300 MHz. The ICP analyzes were performed on an ICP-Spectrociros CCD instrument. Atomic absorption analyses were carried out on a Shimadzu 120 spectrophotometer.

2.1. *Synthesis of chloropropylated MCM-41, MCM-41-Cl*

To a solution of 3-chloropropyl(trimethoxy)silane (10 mmol, 1.98 g) in toluene (40 mL) was added MCM-41 (2.0 g) with stirring under reflux for 24 h. The chloropropylated

MCM-41 (MCM-41-Cl) was filtered, washed with Et_2O and dried under vacuum at 50°C overnight.

2.2. *Synthesis of ionic liquid-modified MCM-41, MCM-41-Im*

To a suspension of chloropropylated MCM-41 (1 g) in CH_3CN (20 mL) was added *N*-methylimidazole (10 mmol) and stirred under reflux for 48 h. After the reaction was completed, the MCM-41-Im was filtered, washed consecutively with water and acetone, and dried under vacuum at 70°C overnight.

2.3. *Preparation of PVMo immobilized on ionic liquid-modified MCM-41, PVMo@MCM-41-Im*

To a solution of $Na_5[PMo_{10}V_2O_{40}]$ (1 g) in a mixture of water/acetone (30 mL, 1 : 1 v/v) was added MCM-41-Im (4 g) and refluxed for 24 h. Finally, the catalyst was filtered and dried at room temperature.

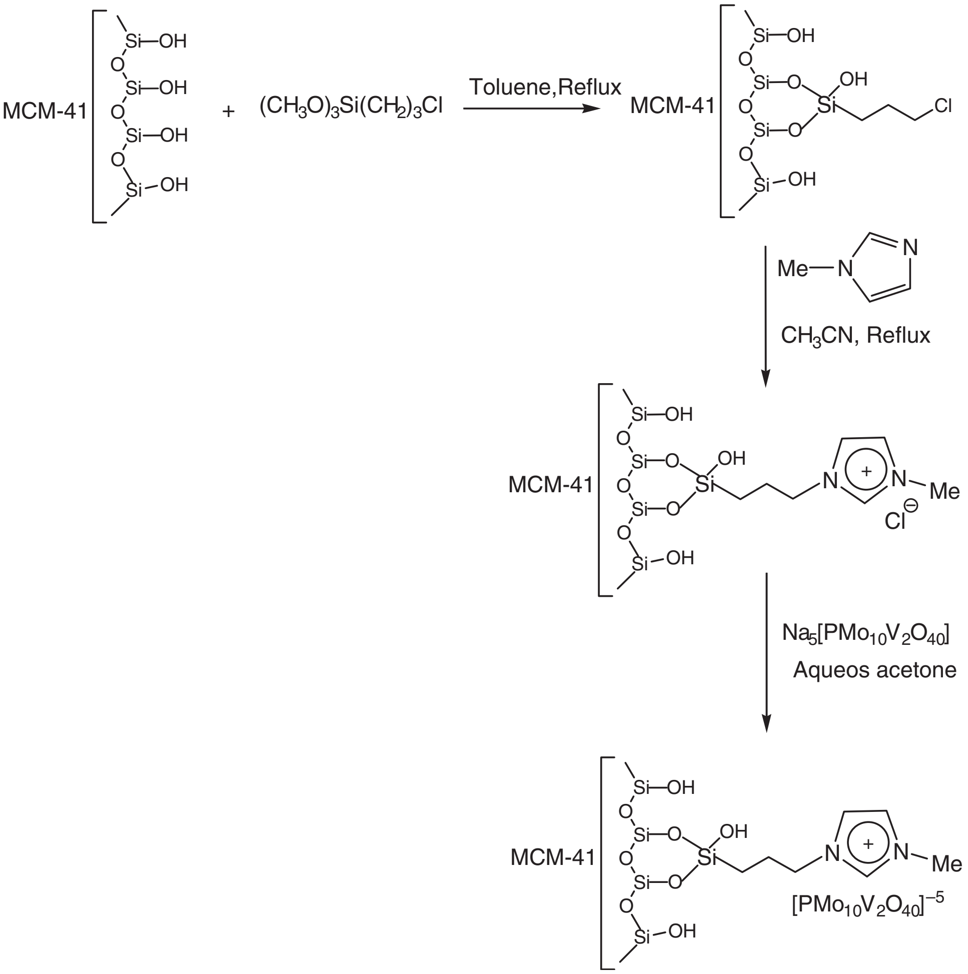
2.4. *General procedure for epoxidation of alkenes with tert-BuOOH catalyzed by PVMo@MCM-41-Im under reflux*

In a 25 mL round-bottom flask equipped with a magnetic stirring bar, to a mixture of alkene (0.5 mmol) and PVMo@MCM-41-Im (50 mg, 0.003 mmol) in 1,2-dichloroethane (5 mL) was added *tert*-BuOOH (0.005 mmol) and refluxed. The progress of the reactions was monitored by GC. At the end of the reaction, the catalyst was filtered and washed with Et_2O (20 mL). The organic layer was separated, concentrated and after chromatography on a short column of silica gel the pure product was obtained. IR and ^1H NMR spectral data confirmed the identities of the products.

3. Results and discussion

3.1. *Preparation and characterization of catalyst, PVMo@MCM-41-Im*

Scheme 2 shows the preparation procedure for PVMo@MCM-41-Im catalyst. First, MCM-41 was reacted with 3-chloropropyl(trimethoxy)silane in which methoxy groups of silane were replaced by silanol groups to produce MCM-41-Cl. Then, 3-chloropropyl functionalized MCM-41-Cl was reacted with *N*-methylimidazole at 80°C to prepare the supported ionic liquid. The FT-IR spectrum of MCM-41-Im (figure 1) shows the characteristic band of the parent ionic liquid ($\nu_{C=N}$) at 1638 cm^{-1}. The four typical skeletal vibrations of the Keggin polyoxoanions appear at 1063 ($\nu_{P–O}$), 951 ($\nu_{Mo=O}$), 867 and 786 cm^{-1} ($\nu_{M–O–M}$) [39]. Owing to the overlap of 867 cm^{-1} of M–O–M and P–O bands with those of Si–O–Si stretching vibrations of mesoporous support, only the bands corresponding to (Mo=O and Mo–O–Mo) are discernable after immobilization on the support (figure 2a). FT-IR spectra indicated that PVMo had been successfully supported on ionic liquid-modified MCM-41. Diffuse reflectance (DR) UV-Vis spectra of PVMo showed a broad absorption peak at 304 nm, which was associated with



Scheme 2. The preparation route for catalyst.

octahedral Mo^{6+}, and can be attributed to a ligand metal charge transfer (LMCT) [40]. This absorption appeared in UV-Vis spectra of PVMo@MCM-41-Im and since pure MCM-41-Im shows no UV absorption in this area (figure 3). These observations clearly proved the presence of PVMo on the support.

The nitrogen content of the MCM-41-Im was about 3.07%. The results are listed in table 1. According to this value, the amount of the ligand, which was attached to MCM-41, was 1.1 m mol g^{-1} of support. The amounts of Mo and V were measured by ICP. Both values showed that the catalyst loading is about 0.06 m mol g^{-1}. The Keggin type PVMo showed diffraction peaks at $2\theta = 8.9°$, 9.8°, 10.3°, 27.4°, and 29.5° [41]. The XRD patterns of MCM-41-Im, PVMo and PVMo@MCM-41-Im are shown in figure 4. From these patterns, it is clear that primary Keggin structure has been introduced in MCM-41-Im. Figure 5 shows SEM images of MCM-41-Im and PVMo@MCM-41-Im. A clear change in the morphology of catalysts indicated that the PVMo has been supported on the MCM-41-Im.

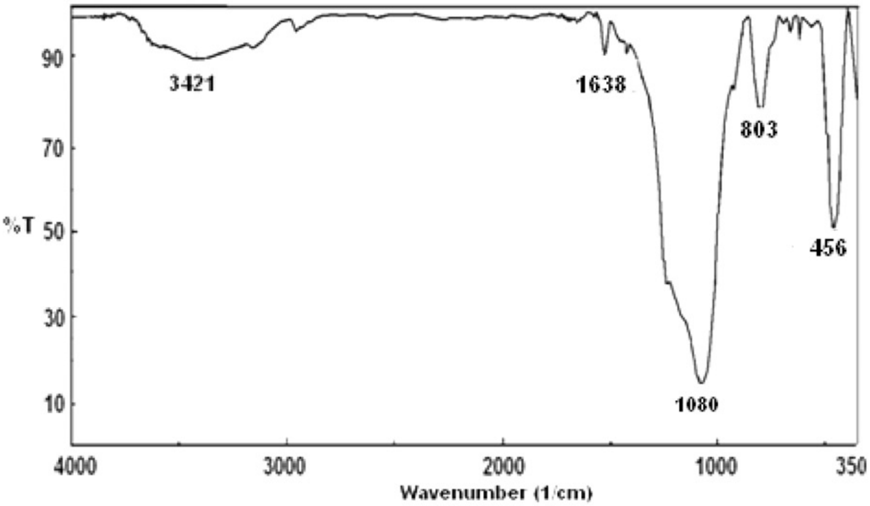


Figure 1. FT-IR spectra of MCM-41-Im.

3.2. *Catalytic activity*

Since heterogeneous catalysts are recoverable, heterogenization of homogenous catalysts is of great interest. Therefore, we decided to immobilize PVMo on MCM-41-Im and investigate its catalytic activity in the epoxidation of various olefins with *tert*-BuOOH under reflux. First, the reaction parameters were optimized in reaction of cyclooctene with TBHP in the presence of PVMo@MCM-41-Im. In order to choose the reaction media, different solvents were checked in the epoxidation of cyclooctene. From 1,2-dichloroethane, dichloromethane, chloroform, carbon tetrachloride, acetonitrile, acetone and methanol, 1,2-dichloroethane was chosen as reaction media because the highest epoxide yield was observed (table 2).

The catalytic activity of this catalyst was investigated in epoxidation of different alkenes (table 3). The reactions were continued until no further progress was observed. In the epoxidation of *cis*-cyclooctene with TBHP, the conversion was 92% with 90% epoxide selectivity and 1,2-cyclooctanediol was produced as by-product. In epoxidation of cyclohexene, the corresponding epoxide was obtained with 79% conversion and 58% epoxide selectivity, and allylic oxidation products (cyclohexene-1-one and cyclohexene-1-ol) were detected in the reaction mixture. In the case of indene, the major product was epoxide. Epoxidation of limonene with 89% conversion and 100% epoxide selectivity led to 74% of 1,2-epoxide and 15% of 8,9-epoxide. In oxidation of α-pinene, the major product was α-pinene oxide (57%), while verbenone and verbenol were produced as minor products. Oxidation of linear alkenes such as 1-octene and 1-heptene was accompanied by allylic oxidation. Blank experiments in the absence of the catalyst were also investigated and the amount of product is negligible.

The catalytic activity of Na_2MoO_4 and $NaVO_3$ supported on MCM-41-Im were also investigated in the oxidation of cyclooctene with TBHP. In the case of

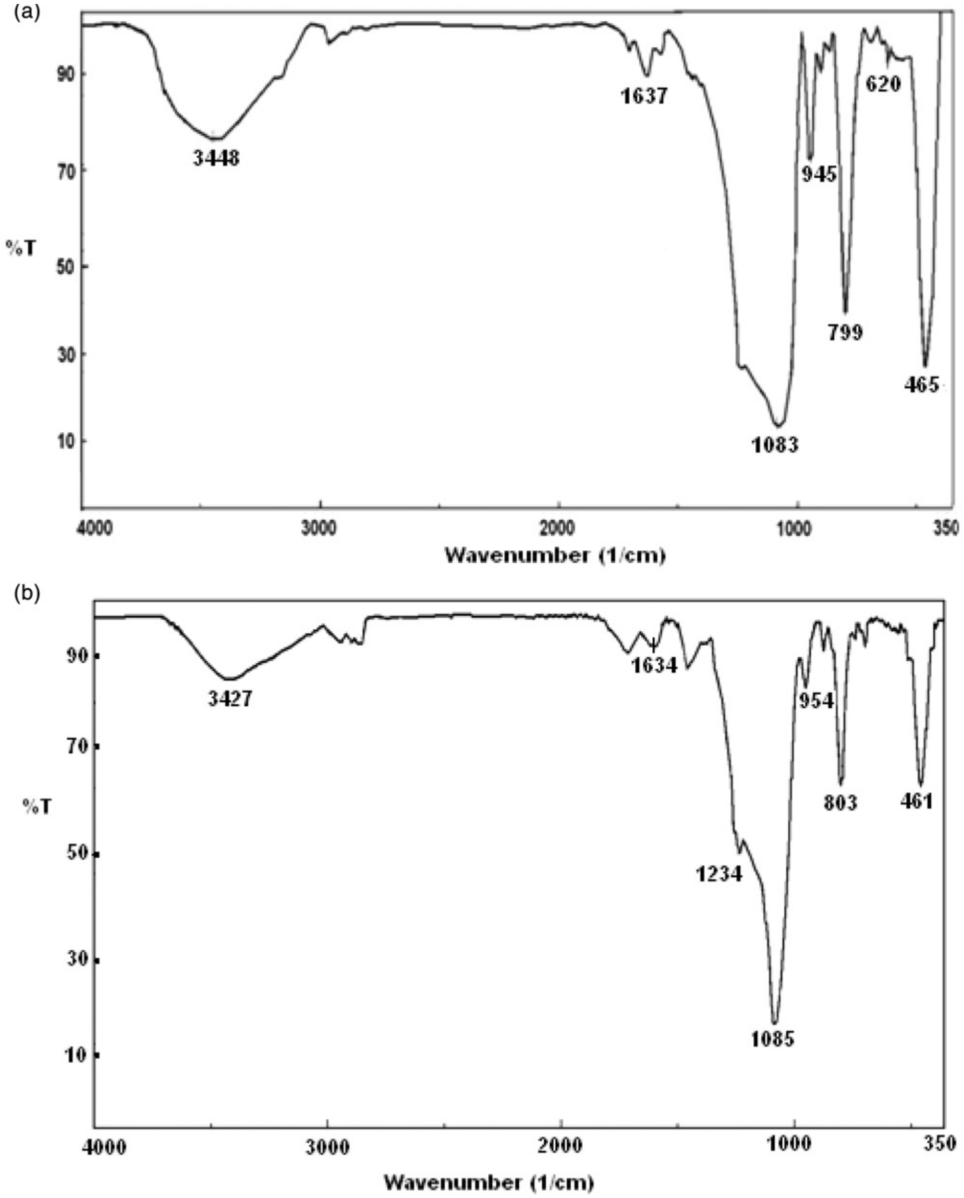


Figure 2. FT-IR spectra of: (a) MCM-41-Im@PVMo and (b) recovered PVMo@MCM-41-Im.

MoO_4@MCM-41-Im, the conversion was 44% and epoxide selectivity was 93%, while in the case of VO_3@MCM-41-Im, the conversion was 8% and the epoxide selectivity was 63%.

Recently, we reported the use of supported PVMo in alkene epoxidation [17–22]. No doubt, all of these methods are good in terms of reactivity and reusability; the present method also has advantages over previous systems such as thermal stability, ease of

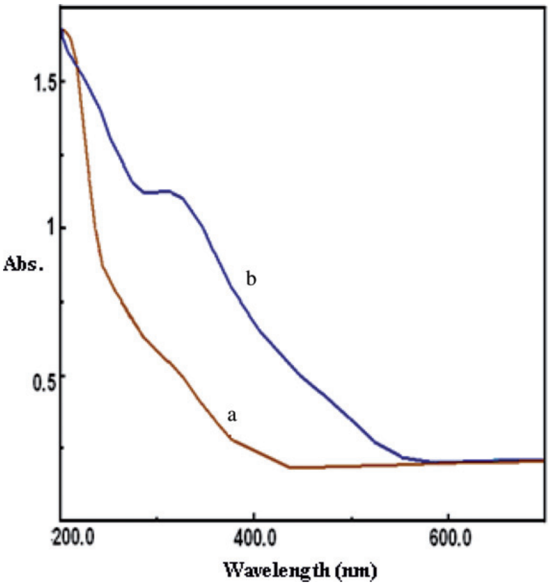


Figure 3. DR UV-Vis spectra of: (a) MCM-41-Im and (b) PVMo@MCM-41-Im.

Table 1. Analytical data of supported ionic liquid and catalyst.

Compound	C (%)	H (%)	N (%)	Mo (%)	V (%)
MCM-41-Im	10.61	1.94	3.07	–	–
PVMo@MCM-41-Im	7.76	1.89	1.24	5.75	0.62

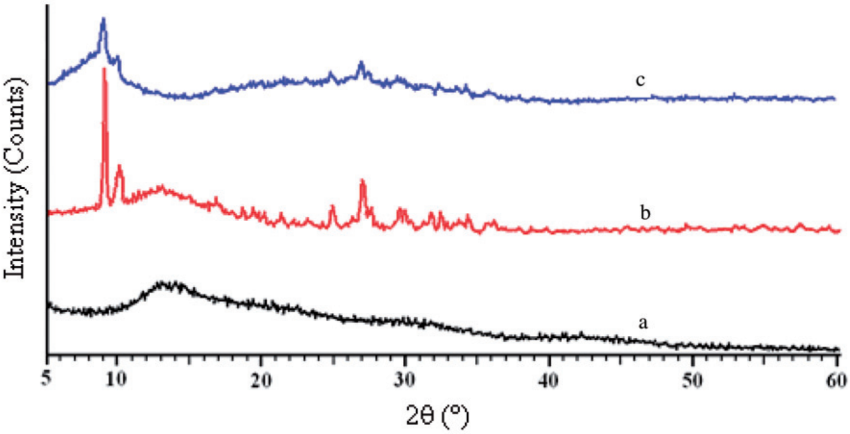


Figure 4. XRD patterns of: (a) MCM-41-Im, (b) PVMo, and (c) PVMo@MCM-41-Im composite.

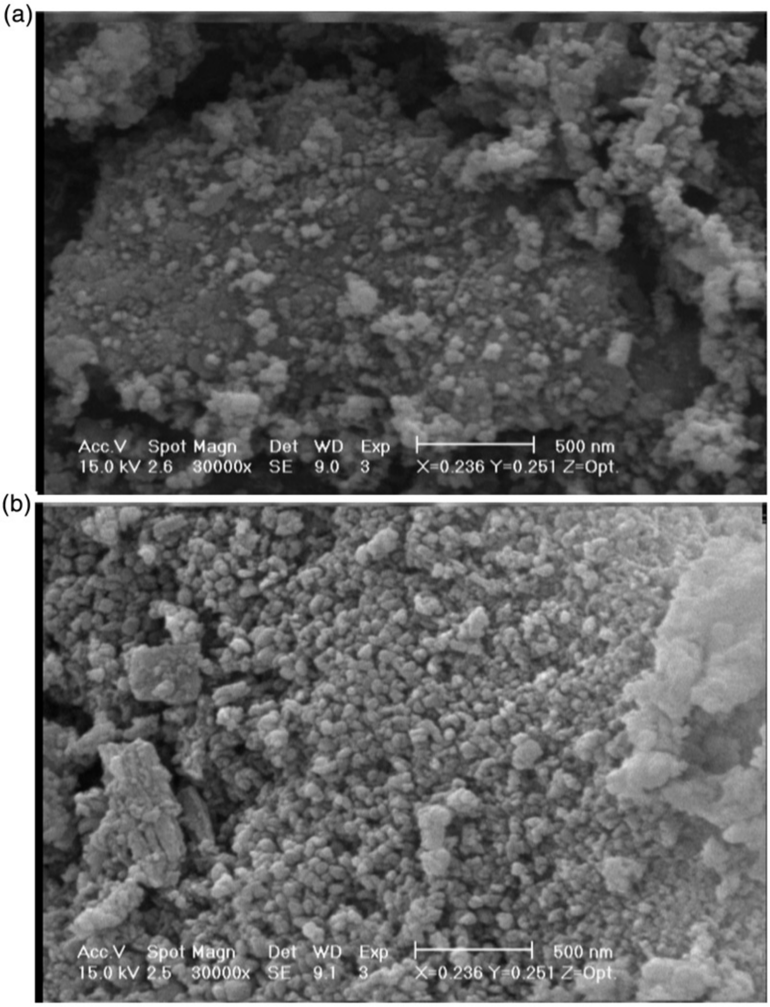


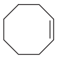
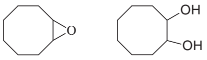
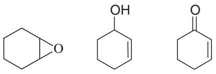
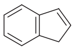
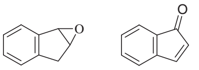
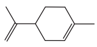
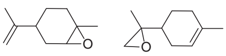
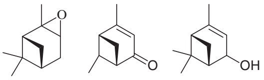
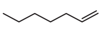
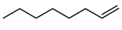
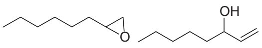
Figure 5. Scanning electron micrographs of: (a) MCM-41-Im and (b) PVMo@MCM-41-Im.

Table 2. The effect of solvent on the epoxidation of *cis*-cyclooctene catalyzed by PVMo@MCM-41-Im under reflux.[a]

Entry	Solvent	Epoxide (%)[b]	Time (h)
1	CH_2Cl_2	6	25
2	$CHCl_3$	21	25
3	$(CH_3)_2CO$	57	25
4	CH_3OH	25	25
5	CH_3CN	30	25
6	$C_2H_4Cl_2$	90	25

[a] Reaction conditions: *cis*-cyclooctene (0.5 mmol), catalyst (50 mg, 0.003 mmol), 5 mL solvent, TBHP (0.005 mmol).
[b] GC yield based on the starting cyclooctene.

Table 3. Oxidation of alkenes with THBP catalyzed by PVMo@MCM-41-Im under reflux.[a]

Row	Substrate	Product	Time (h)	Conversion (%)[b]	Epoxide selectivity (%)	TOF (h^{-1})
1			25	92	90	12.27
2			24	79	58	10.97
3			23	60	40	8.70
4			26	89	100 1,2-epoxide (74%) 8,9-epoxide (15%)	11.41
5			22	65	57	9.85
6			22	70	26	10.61
7			25	92	40	12.27

[a] Reaction conditions: alkene (0.5 mmol), TBHP (0.005 mmol), catalyst (50 mg, 0.003 mmol), 1,2- dichloroethane (5 mL).
[b] GC yield based on the starting alkene.

Table 4. The results obtained from catalyst reuse and stability in the oxidation of cyclooctene with THBP by PVMo@MCM-41-Im under reflux.[a]

Run	Conversion (%)[b]	Time (h)	Mo leached (%)[c]
1	92	25	1.59
2	90	25	0.77
3	90	25	–
4	90	25	–
5	90	25	–
6	90	25	–
7	90	25	–
8	90	25	–
9	90	25	–
10	90	25	–

[a] Reaction conditions: alkene (0.5 mmol), TBHP (0.005 mmol), catalyst (50 mg, 0.003 mmol), 1,2- dichloroethane (5 mL).
[b] GC yield based on the starting alkene.
[c] Determined by AA.

preparation and low cost of the catalyst. On the other hand, this catalytic system is superior in terms of conversion and/or epoxide selectivity.

3.3. *Catalyst reuse and stability*

The reusability of a supported catalyst is one of the most important benefits of heterogeneous catalysts, because transition-metal complexes are often expensive to purchase or prepare. Therefore, heterogenization of homogeneous catalysts makes them useful for commercial applications. To assess stability and reusability, the catalyst was separated from the reaction mixture after each experiment, washed thoroughly with acetonitrile and *n*-hexane successively and dried before being used in the subsequent run. The catalyst was consecutively reused ten times without any loss of its catalytic activity (table 4). The filtrates were used for determination of the catalyst leaching by atomic absorption spectroscopy (AAS). The results showed that in the first two runs some catalyst is leached from support (1.59% in the first run and 0.77% in the second run), but in the next runs no leaching was observed. FT-IR spectroscopy of the recovered catalyst after using for ten times showed no change in its IR spectra (figure 2b).

4. Conclusion

We have prepared a recyclable catalyst based on immobilization of vanadium polyoxometalate on ionic liquid-modified MCM-41 which is an efficient catalyst for epoxidation of alkenes with *tert*-BuOOH. The catalyst could be easily separated from the reaction system and reused.

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