



Encapsulation of Keggin-type phosphotungstic acid into the mesopores of SBA-16 as a reusable heterogeneous catalyst for the epoxidation of olefins

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KEYWORDS

Mesoporous SBA-16;
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 Keggin;
 Immobilization;
 Epoxidation.

Abstract. A heterogeneous catalyst for the epoxidation of olefins was prepared by encapsulating Keggin-type phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) into the mesopores of SBA-16. After the encapsulation, the pore entrance size of SBA-16 was reduced through a silylation method to encompass the catalyst in the mesopores and allow easy diffusion of the reactants and products during the catalytic process. The prepared catalyst was characterized by FT-IR and Inductively Coupled Plasma-Optical Emission Spectroscopies (ICP-OES), X-Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM). The analysis results revealed that the mesoporous nature of SBA-16 was conserved after encapsulation of the catalyst following the silylation step. The catalytic activity of the prepared material was assessed in the epoxidation of olefins with H_2O_2 . The heterogeneous catalyst was recovered and reused up to five cycles without considerable decrease in activity.

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1. Introduction

Polyoxometalates (POMs) are a prominent category of transition metal oxide anions, mostly vanadium, molybdenum, and tungsten with various structures [1-5]. The major utilization of these compounds is in the area of catalysis where soluble POMs exhibit the role of homogeneous catalysts in the oxidation of organic compounds [5-13]. It is well-known that POMs have fast and reversible redox properties, which make them hopeful catalysts for the oxidation of olefins, aromatics, and alcohols [14,15]. So far, due to the green chemistry considerations, many of these catalysts have been explored for the epoxidation of

olefins in the presence of hydrogen peroxide [15-18]. However, the troubles in separation and reuse of these homogeneous catalysts have restricted their large-scale applications in industrial syntheses. In addition, low specific surface area of these compounds in solid state has restricted the accessibility of their active sites and this decreases their catalytic activity in heterogeneous phase. Thus, immobilization of POMs into extremely porous materials is of great attention due to the facile separation and recovery of catalyst in practical uses. Encapsulation of catalytically active POMs into suitable porous supports is a useful approach for designing efficient heterogeneous catalysts and a variety of porous materials have been used for this purpose [19]. Metal-Organic Frameworks (MOFs) have been used as supports for the immobilization of POMs [20-25]. However, the difficulties in their preparation on the one hand and their low stability in some reaction media on the other hand have limited their wide utilization in heterogeneous catalysis. There are also some reports

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on the encapsulation of Keggin-type POMs into the supercages of zeolite Y [26-30]. But, as the size of the Keggin structures is larger than that of the pore entrance of zeolite Y, they cannot enter pore channels and serious leaching of POMs into the reaction mixture has been observed, which leads to their poor reusability in catalytic uses [27].

As the size of the pore entrance must be sufficiently large to accommodate the POMs molecules into the pores of porous materials, many attempts have been made for the encapsulation of POMs inside the pores of some mesoporous materials, especially SBA-15 [31-37] and MCM-41 [37-44]. The encapsulation of Keggin-type POMs inside the pores of mesoporous molecular sieves may provide active catalysts for desired reactions. However, the attachment of POMs to the mesopore walls takes place by means of very weak interaction of the POMs acidic protons with the silanol groups and gives rise to the leaching of the POMs when using these systems in polar solvents. Kozhevnikov and van Bekkum reported high catalytic activity of heteropoly acid-mesoporous systems for acid catalyzed reactions conducted in the liquid phase [45-47]. Nevertheless, they indicated that during the reactions involving polar media, POMs were delivered from mesopores and the catalytic reaction continued in homogeneous phase. Considering the above-mentioned drawbacks, we want to report an efficient method for designing an active and stable heterogeneous epoxidation catalyst by encapsulating the POMs in the mesopores of SBA-16 material.

Recently, SBA-16 mesoporous material has attracted much attention as support of heterogeneous catalysts due to its uniform and large pores, high surface area, high thermal stability, and tunable pore size [48-52]. It has a three-dimensional cubic mesoporous structure and, due to its large nanocages, it is a promising support for the encapsulation of POMs. While the immobilization of POMs catalysts on mesoporous materials such as SBA-15 and MCM-41 has been widely reported [31,44], to the best of our knowledge, there are few reports devoted to the immobilization of POMs into the mesoporous SBA-16 without investigating its catalytic activity and stability [37,53,54].

In this work, Keggin-type 12-tungstophosphoric acid is confined in the nanocages of SBA-16 by encapsulation and reducing the pore entrance size through the silylation method. Since there are no covalent linkage and other strong interactions between the heteropoly acid and the wall surface, the encapsulated catalyst in the nanocages keeps its primary properties as much as possible. The prepared heterogeneous catalyst is used for the epoxidation of olefins in the presence of H_2O_2 . Finally, the stability of the prepared heterogeneous catalyst in the reaction conditions is investigated.

2. Experimental

2.1. Materials and methods

Pluronic copolymer F-127 ($EO_{106}PO_{70}EO_{106}$) was purchased from Sigma-Aldrich. All of the other reagents were provided from Merck Company and used without additional purification. FT-IR spectra of the materials were acquired using Perkin-Elmer Spectrum RXI FT-IR spectrometer. The amount of the polyoxometalate in samples was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) on VARIAN VISTA-MPX after dissolving the samples in hydrogen fluoride. The powder X-ray diffraction patterns of the synthesized materials were recorded on a SIEFERT XRD 3003 PTS diffractometer using $Cu\ K\alpha$ radiation (wavelength, $\lambda = 0.154\text{ nm}$). Transmission Electron Microscopy (TEM) analysis was performed using a Philips EM 208 S instrument with an accelerating voltage of 100 kV. The reaction products of the catalytic tests were analyzed by gas chromatography (Agilent Technologies 6890N, HP-5 capillary column) with Flame Ionization Detector (FID) using helium as carrier gas.

2.2. Preparation of the catalyst

The SBA-16 mesoporous material and $H_3PW_{12}O_{40}$ were synthesized according to the methods in the literature.^{49,5} The heterogeneous catalyst was prepared by the following method: 500 mg of calcined SBA-16 was dispersed in a solution of 0.1 mmol $H_3PW_{12}O_{40}$ in 10 ml water and the mixture was stirred for 24 h at room temperature. The excess water was slowly vaporized and the solid dried in vacuum oven overnight at 100°C. Based on the method in the literature [50], the modification and adjusting the pore entrance size of SBA-16 were performed by silylation reaction. The obtained solid was dispersed in 1.5 ml dry toluene, followed by the addition of 1.25 ml anhydrous pyridine and 5 mmol triethoxyoctylsilane, and then refluxed for 24 h under nitrogen atmosphere. After filtration, the white precipitate was washed with CH_2Cl_2 to eliminate the unreacted triethoxyoctylsilane and then dried in vacuum overnight. The precipitate was Soxhlet extracted with distilled water to remove the physisorbed polyoxometalate species and then dried in vacuum oven for 24 h.

2.3. Catalytic studies

100 mg of catalyst (activated in vacuum oven at 120°C overnight) was dispersed in a solution of 8 mmol of olefin in 10 ml of acetonitrile. After addition of 1.5 ml 30% H_2O_2 (12.8 mmol) and isooctane (8.75 mmol, as internal standard), the reaction mixture was refluxed under nitrogen atmosphere. Gas chromatography was employed to monitor the progress of the reaction in appropriate times. On the completion of the reaction, the catalyst was separated, washed with CH_2Cl_2 , and

after activation in vacuum oven was reused in the next run.

3. Results and discussion

3.1. Immobilization of the phosphotungstic acid into the mesopores of SBA-16

Immobilization of Keggin-type phosphotungstic acid (PTA) into the mesopores of SBA-16 was achieved with encapsulation method. Due to the larger pore entrance size of SBA-16 than the size of PTA molecules, the leaching of the PTA molecules out of the mesopores during the catalytic reactions is probable. Hence, the pore entrance size of SBA-16 should be adjusted to be small enough to inhibit the escape of PTA molecules from the mesopores. For this purpose, the prepared material in the first step was reacted with triethoxyoctylsilane to modify the pore entrance size of the SBA-16. Earlier work by Li et al. showed that silylation with this reagent resulted in reducing the pore entrance rather than pore blocking [50].

3.2. Characterization of the prepared material

In order to approve the immobilization of the PTA into the mesopores of SBA-16, the FT-IR spectra were acquired and studied. FT-IR spectra of pure PTA, SBA-16, and encapsulated PTA into the mesopores of SBA-16, PTA@SBA-16, are shown in Figure 1. In the FT-IR spectrum of pure PTA Figure 1(a), the band at 1080 cm^{-1} is attributed to the P=O asymmetric vibration of PO_4 unit, whereas the bands at 982, 893, and 798 cm^{-1} are assigned to the stretching modes of the terminal W=O, edge sharing $\text{W-O}_e\text{-W}$, and corner sharing $\text{W-O}_c\text{-W}$ units, respectively [55]. The FT-

IR spectrum of pristine SBA-16 Figure 1(b) exhibits the asymmetric and symmetric stretching vibrations of Si-O-Si at 1076 cm^{-1} and 808 cm^{-1} , respectively [49,53]. In the FT-IR spectrum of PTA@SBA-16 Figure 1(c), the characteristic bands of Keggin-type phosphotungstic acid in PTA@SBA-16 are similar to those of the unsupported one. The P=O stretching band in the PTA@SBA-16 sample is not clearly identified due to the overlap with the broad Si-O-Si band at 1079 cm^{-1} . However, the bands at 981, 896, and 806 cm^{-1} are clearly observed for PTA@SBA-16, which can be attributed to the stretching modes of the terminal W=O, edge sharing $\text{W-O}_e\text{-W}$, and corner sharing $\text{W-O}_c\text{-W}$ units of phosphotungstic acid, respectively. The observation of these bands after soxhlet extraction of the prepared material and elimination of physisorbed species indicates that phosphotungstic acid species are successfully entrapped into the SBA-16 support. On the other hand, the peaks in the range of $2800\text{-}3000\text{ cm}^{-1}$ are due to C-H stretching vibrations of octyl groups, confirming the successful silylation of the material. The decrease in the intensity of the broad band in the range of $3200\text{-}3700\text{ cm}^{-1}$ indicates that a portion of silanol groups is consumed due to the silylation reaction.

ICP-OES measurements show that the soxhlet extracted PTA@SBA-16 material contains 0.069 mmol phosphotungstic acid per gram of SBA-16 and, further, approve its encapsulation into the mesopores of SBA-16.

Low-angle powder X-Ray Diffraction (XRD) patterns of SBA-16 and PTA@SBA-16 are shown in Figure 2. The comparison of the patterns indicates the structural preservation upon encapsulation of PTA molecules. Immobilization of the PTA molecules into the mesopores of SBA-16 host reduces the order of mesostructured system. Thus, a decrease in the intensity of the peak in the low-angle region is observed. The characteristic peaks of PTA were not observed in the wide angle region, which can be ascribed to the fine

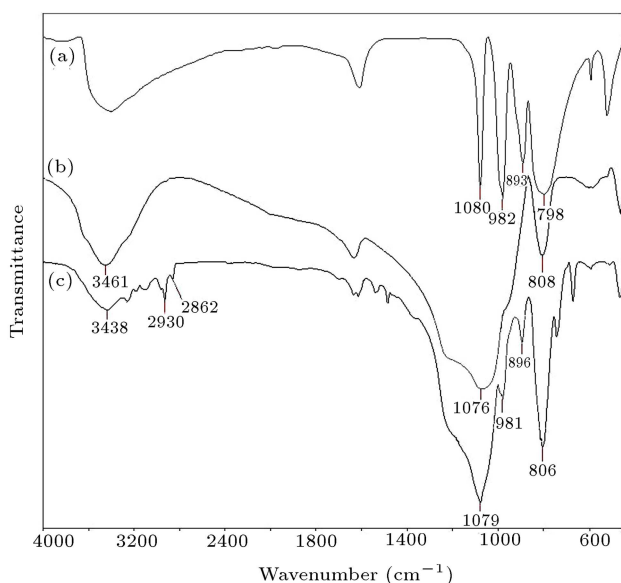


Figure 1. FT-IR spectra of (a) phosphotungstic acid, (b) SBA-16, and (c) PTA@SBA-16.

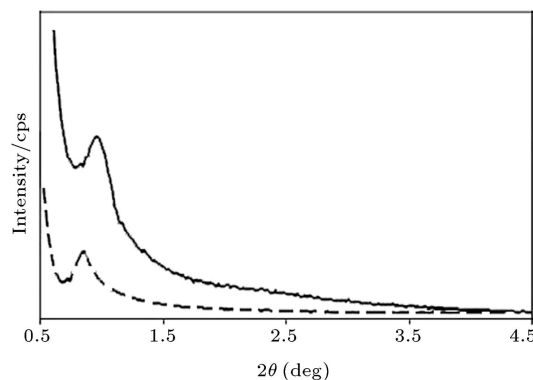


Figure 2. XRD patterns of SBA-16 (solid line) and PTA@SBA-16 (dashed line).

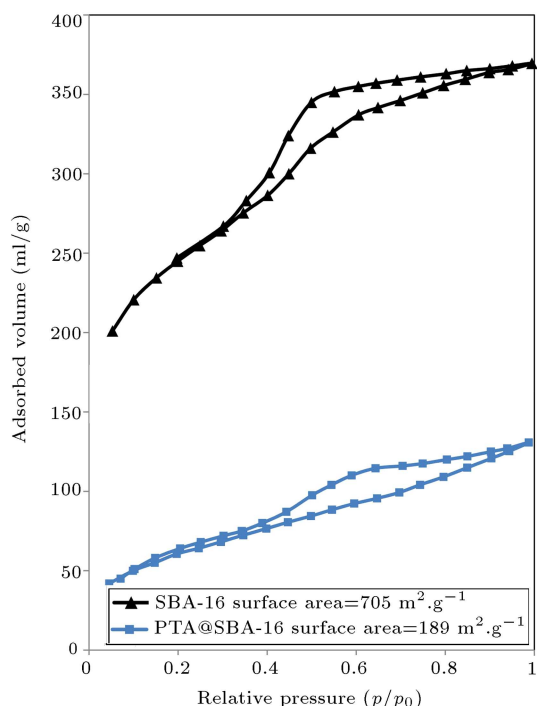


Figure 3. Nitrogen sorption isotherms of SBA-16 and PTA@SBA-16.

dispersion of the PTA species within the mesopores of SBA-16.

To explore the changes in the pore structure of SBA-16 after encapsulation of PTA species, N_2 adsorption-desorption experiment was carried out at liquid N_2 temperature; the isotherms are shown in Figure 3. As can be seen, pristine SBA-16 shows type IV isotherm with H_2 hysteresis loop in compliance to the Brunauer-Deming-Deming-Teller (BDDT) classification, which is characteristic of a cage-like cubic mesoporous structure [48,49]. The PTA@SBA-16 also shows type IV isotherm with H_2 hysteresis loop, approving that this material still preserves the cubic cage-like mesoporous structure of the SBA-16. In comparison with SBA-16, adsorbed volume of PTA@SBA-16 decreases, which indicates that the pore size is reduced by encapsulation of PTA molecules.

The surface areas of the materials were obtained by BET (Brunauer, Emmett, and Teller) method (as indicated in the Figure 3). It was found that in comparison with pristine SBA-16, the surface area of the PTA@SBA-16 sample decreased, which confirmed the presence of PTA species in the mesopores of SBA-16.

Transmission Electron Microscopy (TEM) analysis was applied to investigate the extent of order in PTA@SBA-16 as well as the uniformity of mesopores (Figure 4). The pore diameter of the sample estimated from the TEM image measures about 4 nm. The TEM micrograph demonstrates that the ordered channel structure of SBA-16 has been preserved after encapsulation of PTA molecules.

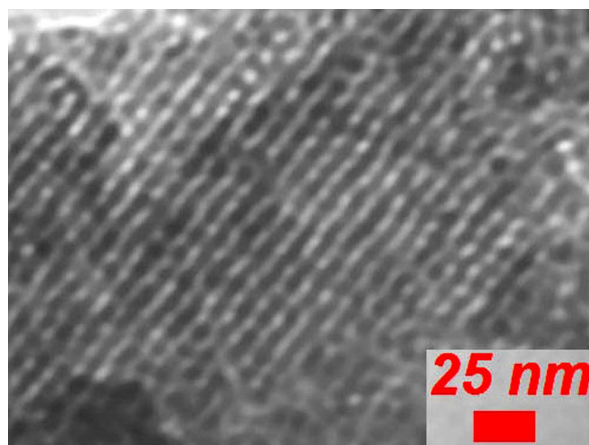


Figure 4. TEM image of the prepared PTA@SBA-16.

3.3. Catalytic activities of the prepared catalyst

The catalytic performance of the resultant PTA@SBA-16 was assessed in the epoxidation of olefins and allylic alcohols using aqueous 30% H_2O_2 . Firstly, the effect of various amounts of H_2O_2 on the epoxidation of cyclooctene was studied of which the results are shown in Table 1. As can be seen, the conversion of cyclooctene increases with increase in the H_2O_2 :cyclooctene ratio. Due to the nonproductive decomposition of H_2O_2 in the course of the reaction, it is required to use excess value of H_2O_2 with respect to the olefins. Thus, the epoxidation reactions were conducted with H_2O_2 :olefin ratio of 1.6:1 of which the results are shown in Figure 5.

The catalytic system was found to be highly active and selective (close to 100%) toward the epoxide formation. As seen in Figure 5, the olefins with higher electronic density of the double bond were more reactive in the epoxidation reaction. Based on the epoxidation mechanism (Figure 6) suggested in literature [56,57], higher electron donating ability of olefin double bond is predicted, hence accelerating the rate of epoxidation. As shown in the proposed mechanism of epoxidation reaction, the active site in the catalyst (peroxygen

Table 1. Investigation of the effect of the amount of hydrogen peroxide on the catalytic epoxidation of cyclooctene.

Run no.	H_2O_2 (mmol)	Conversion ^a (%)	Selectivity ^b (%)
1	8	46	>99
2	10	59	>99
3	12.8	74	>99

Reaction conditions: Catalyst: 100 mg, Cyclooctene: 8 mmol, refluxing: CH_3CN 10 ml, time: 8h.

^a Based on consumed cyclooctene;

^b Selectivity toward epoxyoctane.

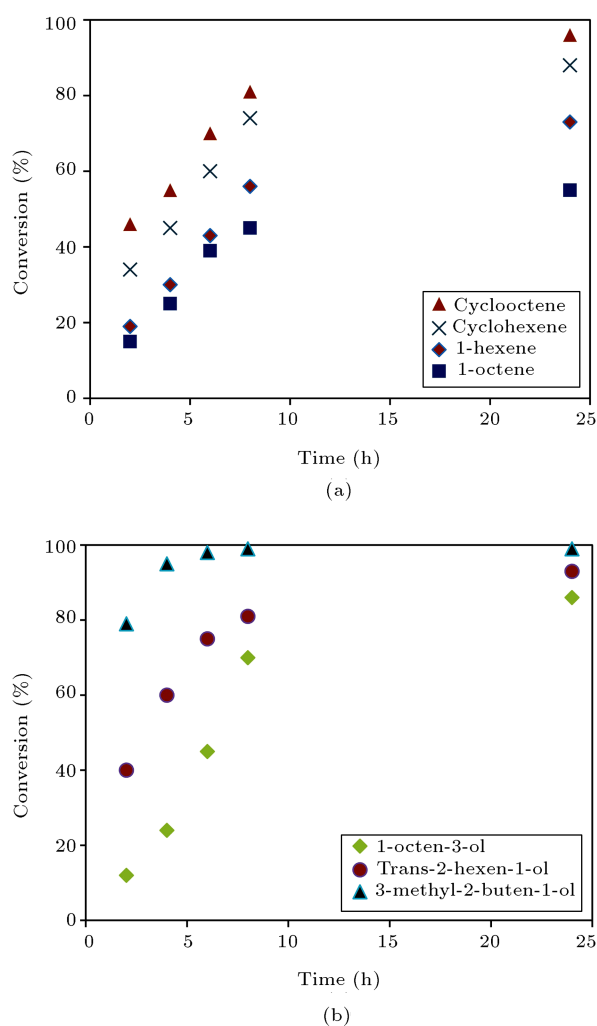


Figure 5. Results of catalytic epoxidation of some olefins and allylic alcohols with H_2O_2 in the presence of PTA@SBA-16. Reaction conditions: Catalyst (100 mg), Olefin (8 mmol), H_2O_2 (12.8 mmol), refluxing CH_3CN (10 ml).

center) has electrophilic character and the mechanism of oxygen transfer to the olefin is electrophilic attack of electron deficient oxygen to the olefin double bond as nucleophilic species. Therefore, more nucleophilic character of the double bond promotes the epoxidation reaction. On the other hand, due to the participation

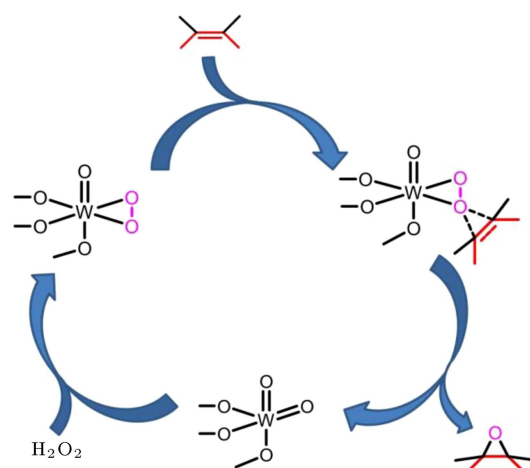


Figure 6. Mechanism of epoxidation of olefins with H_2O_2 in the presence of PTA@SBA-16.

of hydroxyl group in drawing the double bond toward the electrophilic peroxygen center, allylic alcohols are more reactive than simple olefins.

Blank reaction (without the catalyst) was also carried out to specify the role of the catalyst (Table 2). Very low conversion was achieved in the absence of catalyst. Similar epoxidation reaction was carried out with pristine SBA-16 and negligible catalytic activity was evidenced. These results confirm the catalytic effect of the immobilized phosphotungstic acid.

The catalytic properties of the prepared heterogeneous catalyst (PTA@SBA-16) were compared with those of the corresponding homogeneous analogue, i.e. phosphotungstic acid, under the same reaction conditions (Table 2). As can be seen in this table, the reaction rate by using of the prepared heterogeneous catalyst was comparable to that by using the homogeneous one. The results indicate that catalytic performance of the heterogeneous catalyst is related to fine dispersion of the active catalytic species within the mesopores of SBA-16.

On the other hand, in order to evaluate the probable catalytic contribution of the leached PTA species in the epoxidation of cyclooctene, the reaction mixture was filtered off after 2 h and the filtrate was left to react for a further 24 h. As can be seen in

Table 2. Epoxidation of cyclooctene with H_2O_2 in different conditions.

Run no.	Catalyst	Catalyst amount (mg)	Time (h)	Conversion (%)	Selectivity ^a (%)
1	SBA-16	100 mg	24	12	62
2	–	–	24	5	56
3	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	10 mg	2	18	> 99
			8	70	> 99
			24	97	> 99

Reaction conditions: Cyclooctene: 8 mmol, H_2O_2 : 12.8 mmol, refluxing CH_3CN : 10 ml.

^aSelectivity toward epoxyoctane.

Table 3. Investigation of the catalytic contribution of the possibly solubilized heteropoly acid species.

Run no.		Time (h)	Conversion (%)	Selectivity ^a (%)
1	Before filtering the catalyst	2	46	> 99
	After filtering the catalyst	24	50	99

Reaction conditions: Catalyst: 100 mg, cyclooctene: 8 mmol,

H₂O₂: 12.8 mmol, refluxing acetonitrile: 10 ml.

^aSelectivity toward epoxy cyclooctane.

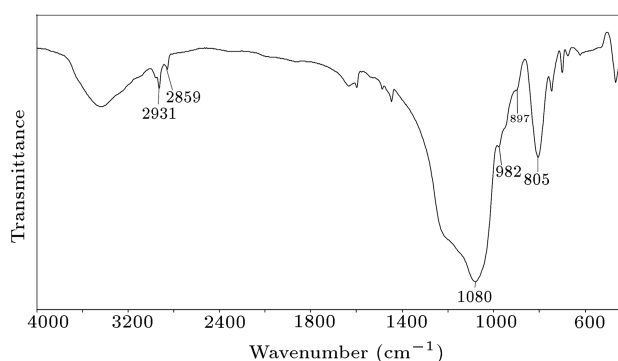
**Figure 7.** FT-IR spectrum of the recovered PTA@SBA-16.

Table 3, in this time span, the conversion of cyclooctene increased by only 4%, suggesting that the epoxidation reaction was nearly stopped by the elimination of the catalyst, and there was no tungsten species in the solution. Moreover, after filtration of the reaction mixture, the solid catalyst was characterized by FT-IR spectroscopy and the tungsten content of the filtrate was also analyzed by ICP-OES. It was found that the quantity of tungsten species in the aqueous phase was negligible. Furthermore, the FT-IR spectrum of the recovered catalyst (Figure 7) showed no change in comparison with fresh PTA@SBA-16 catalyst. Therefore, it can be concluded that the catalytic reaction is really heterogeneous.

The reusability of PTA@SBA-16 was inspected in the epoxidation of 3-methyl-2-butene-1-ol with 30% H₂O₂ of which the results are shown in Figure 8. After each run, the catalyst was isolated from the reaction mixture, washed several times with acetonitrile, and dried before using in the subsequent run. As can be seen in Figure 8, the catalytic activity decreased very slightly during the later runs. Thus, it can be concluded that the catalyst is recoverable and reusable for at least two times in the epoxidation of olefins.

Comparison of these results with our recently published work on the catalyst derived from the immobilization of H₆P₂W₁₈O₆₂ compound with Wells-Dawson structure into the SBA-16 [53], shows that the Keggin-type structure, i.e. PTA@SBA-16, has compa-

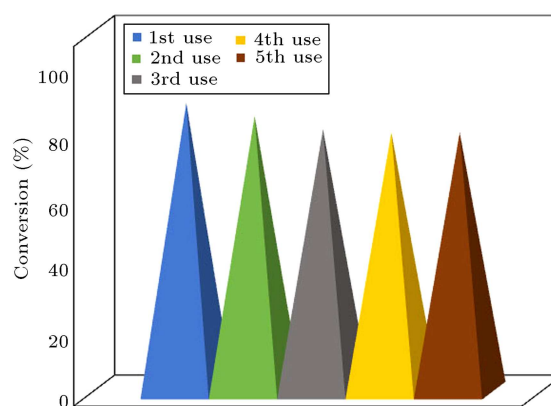
**Figure 8.** Results of catalytic epoxidation of 3-methyl-2-butene-1-ol with H₂O₂ in the presence of recycled PTA@SBA-16. Reaction conditions: catalyst: 100 mg, olefin: 8 mmol, H₂O₂: 12.8 mmol, refluxing CH₃CN: 10 ml

table (e.g., in the case of cyclooctene and cyclohexene) or even higher (e.g., in the case of 1-octene and 1-hexene) activities in the epoxidation of olefins. On the other hand, as the preparation of Keggin-type structure is easier than that of the Wells-Dawson one, the present catalyst is preferred in practical epoxidation of olefins.

4. Conclusion

This work provided an efficient and easy method for immobilization of Keggin-type phosphotungstic acid into the mesopores of SBA-16. The heteropoly acid was confined onto the SBA-16 support by, first, encapsulation and, then, reducing the pore entrance size with silylation reagent. ICP-OES and FT-IR spectroscopies confirmed the immobilization of phosphotungstic acid. XRD and TEM analyses revealed that the structure of mesoporous support was preserved after immobilization of phosphotungstic acid. The prepared material can be efficiently used as active, selective, and environmentally benign catalyst for the epoxidation of olefins. It was shown that the catalyst was really heterogeneous and reusable, which could be used at least two times without considerable loss of activity.

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