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## Supporting $H_5[PMo_{10}V_2O_{40}]$ and $H_5[PW_{10}V_2O_{40}]$ Heteropolyacids onto the Surface of Amine-functionalized Boehmite Nano-particles for Catalytic Epoxidation of Alkenes

Mojgan Jamali<sup>a</sup>, Mahdi Mirzaee<sup>a,\*</sup> and Farrokhzad Mohammadi Zonouz<sup>b</sup>

<sup>a</sup>Faculty of Chemistry, Shahrood University of Technology, Shahrood, Iran

<sup>b</sup>Department of Chemistry, Hakim Sabzevari University, Sabzevar, Iran

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Boehmite nanoparticles were covalently functionalized by 3-(trimethoxysilyl)-propylamine to support  $H_5[PMo_{10}V_2O_{40}]$  and  $H_5[PW_{10}V_2O_{40}]$  Keggin type heteropolyacids. After characterizing these catalysts by FT-IR, PXRD, TG/DTA, CHN, ICP and TEM techniques, they were applied to the epoxidation of *cis*-cyclooctene. The progress of the reactions was investigated by gas-liquid chromatography and the catalytic procedures were optimized for the parameters involved, such as the solvent and oxidant. The results showed that 20 mg of supported  $H_5[PMo_{10}V_2O_{40}]$  catalyst in 2 mL  $C_2H_4Cl_2$  with 0.5 mmol cyclooctene and 1 mmol tert-butyl hydroperoxide at reflux temperature gave 98% yield over 60 min. Recycling experiments revealed that these nanocatalysts could be repeatedly applied up to four times for a nearly complete epoxidation of *cis*-cyclooctene. The optimized experimental conditions were also used successfully for the epoxidation of some other alkenes such as cyclohexene, styrene and  $\alpha$ -methyl styrene.

**Keywords:** Boehmite nanoparticles (BNP), Keggin type heteropolyacids (HPA),  $H_5[PMo_{10}V_2O_{40}]$ ,  $H_5[PW_{10}V_2O_{40}]$

### INTRODUCTION

There is an everyday demand for decreasing the material used and increasing the material produced. This contradiction is also important in chemical catalytic procedures and it is desirable to use less reactant and to obtain more products because of economic and environmental awareness. Therefore the chemical catalytic research encouraged to developing highly efficient catalysts which that could easily and completely be separated from the reaction media. Heteropolyanions (HPA) with superior acidic character are efficient catalysts that were used successfully, in miscellaneous organic reactions such as epoxidation [1]. Supporting HPA on proper solid beds such as cellulose [2], zeolites [3], silica [4], alumina [4], zirconia [4,5], carbon fiber [6], MCM-41 [7], SBA-15 [8],

$Nb_2O_5$  [5] and  $TiO_2$  [5], could improve their catalytic activity by enhancement of their thermal stability and compensate for their low surface area [7]. Impregnation [3-7,9] and adsorption [10] are conventional and simplest methods for supporting HPA on solid catalytic beds. These processes rarely create suitable bonding interactions between HPA and support. Usually, the interaction is weak and the adsorbed HPA could simply elute from the surface of adsorptive, especially in polar solvents. In contrast, when the interaction is strong, the HPA structure may be destroyed [2,4-5]. Therefore, it is desirable to use a chemical bond to support HPA on catalytic beds. There are only two reports bonded supporting of HPA on a solid support. First, Fu *et al.* have been used amine-modified cellulose for the immobilization of  $H_3PW_{12}O_{40}$  (HPW) [2]. This catalyst was used in the transesterification of yellow horn oil. The next is previous research of Mirzaee *et al.*, which used amine-functionalized boehmite nanoparticles (AFBNP) to support Keggin-type HPA of  $H_3[PMo_{12}O_{40}]$ ,

\*Corresponding author. E-mail: [mmirzaee@shahroodut.ac.ir](mailto:mmirzaee@shahroodut.ac.ir)

$H_3[PW_{12}O_{40}]$ ,  $H_4[SiMo_{12}O_{40}]$  and  $H_4[SiW_{12}O_{40}]$  through effective electrostatic interaction. The HPAs that immobilized on boehmite were used for epoxidation of different alkenes [11]. In continuation of this study, here we used vanadium containing HPAs,  $H_5[PMo_{10}V_2O_{40}]$  and  $H_5[PW_{10}V_2O_{40}]$ , to support on AFBNP to evaluate the role of vanadium in epoxidation of alkenes.

Boehmite ( $\gamma$ -AlOOH) nano-particles (BNP) are inorganic-insoluble solid support, which contained extra hydroxyl groups on its surface. These groups on the one hand make it a good candidate to catalyze some organic reactions [12,13], and on the other hand, prepare a platform for surface modification and functionalization [14-16]. The amine-functional group usually produced by covalent bonding of  $\equiv Si(CH_2)_3NH_2$  through the reaction of BNP [14-16] or other hydroxyl covered solid beds with  $(MeO)_3Si(CH_2)_3NH_2$  [17-18]. The covalently anchored amine groups then reacted with vanadium-containing Keggin-type HPA to impound them, through electrostatic interaction. The resulting catalysts were then thoroughly characterized by different techniques including FTIR, XRD, TEM, BET and thermal analysis. Activities of these catalysts were also extensively investigated toward epoxidation of some alkenes.

Epoxides are valuable intermediates to produce commercially important chemicals, such as polymers, pharmaceuticals, food additives, dye-stuffs and fragrance compounds [14]. They are commonly derived by mild and selective oxidation of alkenes and the presence of metal-based catalysts is vital to preserving this condition [14-16]. Conventionally, the epoxidation of *cis*-cyclooctene was used as a model to check and compare the activity of new catalysts with previous ones. Here we tested the activity of our newly prepared catalysts in epoxidation of cyclooctene as well as some other alkenes.

## EXPERIMENTAL

### Materials and Methods

The required solvents and reagents were purchased from Merck or Fluka, and used without further purification. IR spectra were recorded on a Rayleigh WQF-510A FT-IR instrument at  $4\text{ cm}^{-1}$  resolution using KBr pellets. Thermo-

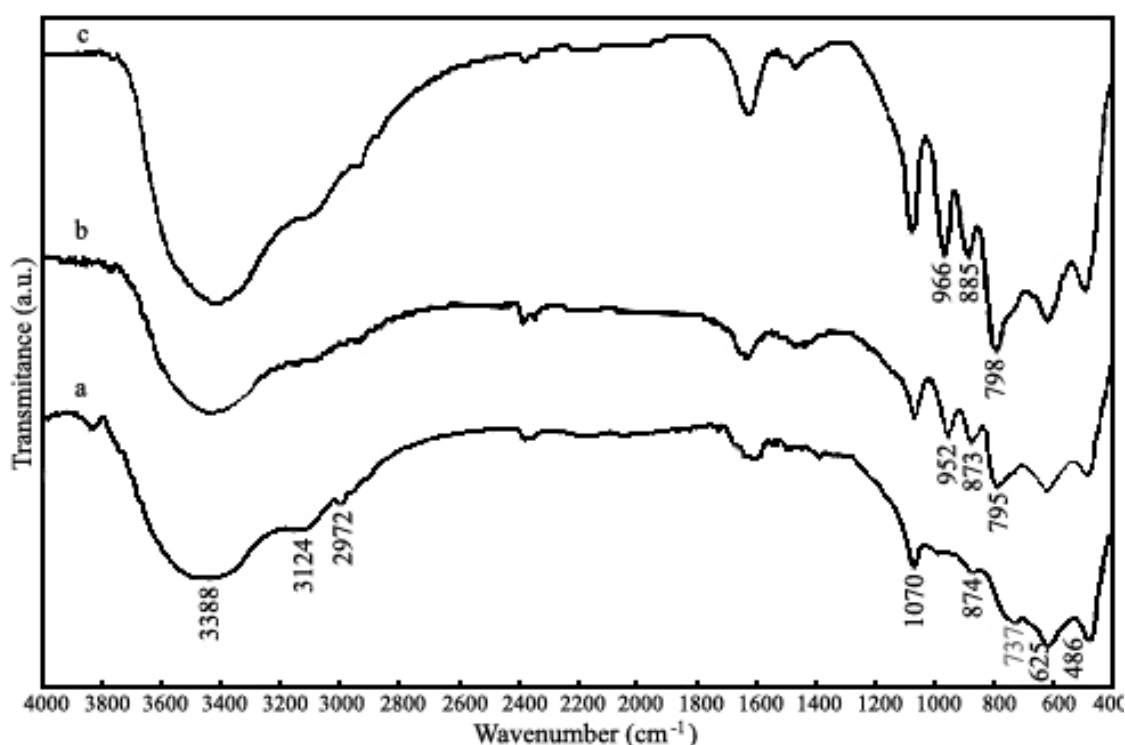
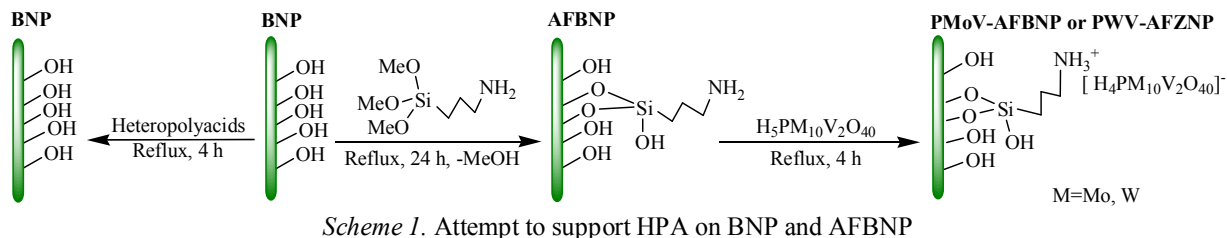
gravimetric analyses were carried out on a NETZSCH STA 409 PC Luxx with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in air. Elemental analyses were carried out on a LECO TruSpec CHNS Analyzer. Electron microscopy was performed on a VEGA TESCAN-LMU scanning electron microscope. Gas-liquid chromatography (GLC) was carried out on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200.

### Preparation of Supported Heteropolyacids Catalysts

Boehmite nano-particles (BNP) [19] and amine-functionalized boehmite nano-particles (AFBNP) [15] were prepared according to earlier reports. Keggin types heteropolyacids:  $H_5[PMo_{10}V_2O_{40}]$  (HPMoV) and  $H_5[PW_{10}V_2O_{40}]$  (HPWV) were prepared according to the literature reports [20]. The prepared HPAs were used to load on BNP or AFBNP. For this purpose, 0.35 mmol of each heteropolyacid was dissolved in 30.0 mL ethanol, individually. Then 1.00 g of dry BNP or AFBNP was added to each solution, and the mixture was subsequently refluxed for 4 h. The mixture was then cooled down and filtered off, and the resulting precipitate was washed several times with ethanol and dried at  $100\text{ }^\circ\text{C}$  overnight. The ICP analysis showed that 0.32 and 0.31 mmol HPA anchored on 1.00 g PMoV-AFBNP and PWV-AFBNP, respectively. According to the ICP analysis HPA did not anchor on BNP.

### Catalytic Epoxidation of Alkenes

In a typical process, an appropriate round bottom flask equipped with a magnetic stirrer bar and a condenser was charged with an alkene, an oxidant, the catalyst (PMoV-AFBNP or PWV-AFBNP), and solvent, and the mixture were then refluxed. All the reactions were performed at least two times, and the reaction progress was monitored by GLC. Since different alkenes have different reactivity toward oxidation, these reactions were continued until no further progress was observed. The characterizations of the main products and by-products were performed by comparison of their retention times with those for the standard samples. The alkene conversions and product selectivity were calculated using their peak areas by the standard addition method.



**Fig. 1.** FT-IR spectra of a) AFBNP, b) PMoV-AFBNP and c) PWV-AFBNP.

### Catalyst Recycling

In a typical experiment, after recovering the catalyst from the reaction mixture at the optimum experimental conditions, it was washed several times with  $C_2H_4Cl_2$  and then used in the same procedure under the same conditions.

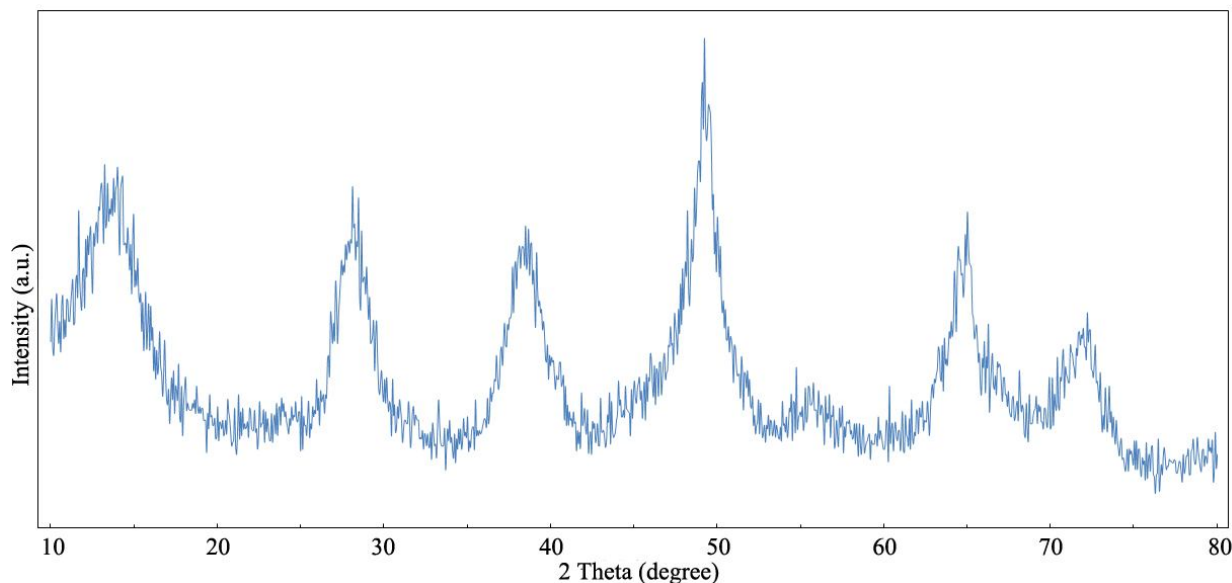
### RESULTS AND DISCUSSION

BNP was grafted with MSPA since they showed no acceptable interaction with HPA (Scheme 1). The supported catalysts were then used in the epoxidation of *cis*-cycloocten, and the catalytic procedures were optimized for

the parameters involved such as the catalyst, solvent, and oxidant (Table 1). Hot filtration was also used to confirm the heterogenic character of both catalytic procedures. Then they were used for the epoxidation of different alkenes under the optimum experimental conditions (Table 2). In addition, recycling experiments were carried out to reveal the reusability of these catalysts (Table 3).

### Preparation and Characterization of Supported Heteropolyanions on BNP and AFBNP

It was proved that, for an efficient epoxidation of alkenes in mild conditions, the presence of a catalyst



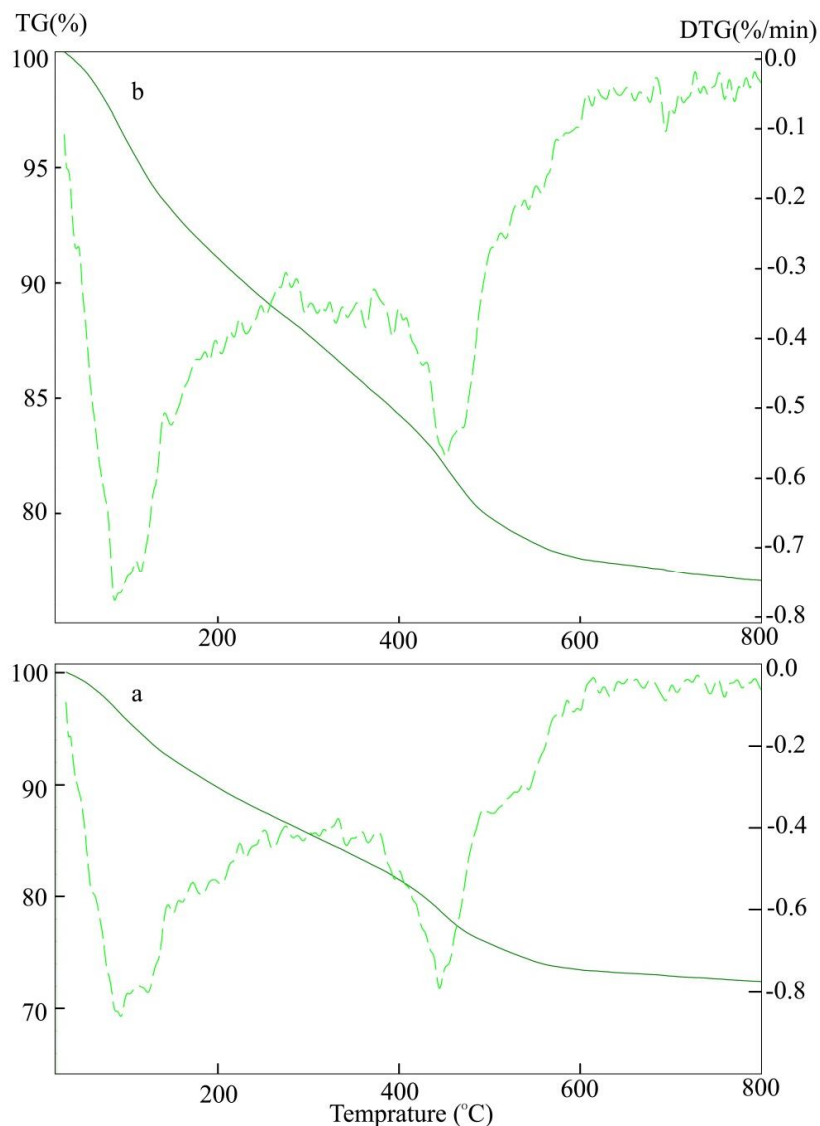
**Fig. 2.** PXRD pattern of BNP.

containing an active metal site was vital because the oxidant could coordinate to this site, and be activated for the epoxidation process. However, BNP and AFBNP [11,14-16] showed no reactivity in the epoxidation of alkenes. Furthermore, supporting the vanadium free [11] and vanadium containing (Scheme 1) heteropolyacids on BNP failed. The IR spectra and ICP analyses showed no evidence that could confirm an acceptable interaction between them even after 4 h reflux. Consequently, in continuation of our studies on use of AFBNP which contain pending  $\equiv\text{O}_3\text{Si}(\text{CH}_2)_3\text{X}$  ( $\text{X} = \text{NH}_2$  or  $\text{Cl}$ ) groups to support metal complexes [14-16] and HPA [11], here we tried to support vanadium containing Keggin type HPA on the surface of AFBNP (Scheme 1). For this purpose, PMoV or PWV were refluxed with AFBNP in ethanol for 4 h. This process resulted in the formation of the quaternary ammonium cations by proton transfer from HPA to the grafted amine groups on the surface of AFBNP which attract the HPA *via* electrostatic interactions (Scheme 1).

Figure 1 shows the FT-IR spectra of AFBNP and supported HPA on AFBNP. All of them clearly contain the characteristic vibration bands of BNP at 3380 and 3075  $\text{cm}^{-1}$ , which were assigned to the bridged and terminal hydroxyl groups of BNP, respectively [20]. These stretching

vibrations were accompanied by a bending vibration at 1070  $\text{cm}^{-1}$  [20]. BNP also had some distinguishable Al-O related vibrations at about 740, 620, and 480  $\text{cm}^{-1}$  in the IR spectrum [23]. The IR spectrum for AFBNP (Fig. 1a) showed a new band at 2972  $\text{cm}^{-1}$  in addition to the BNP characteristic bands, which was assigned to the aliphatic C-H stretching vibration of the grafted amine groups [11,14-15]. The N-H stretching vibration over 3000  $\text{cm}^{-1}$  was covered by broad bands of BNP hydroxyl group vibrations in this region [11,14-15]. The IR spectrum for PMoV-AFBNP (Fig. 1b) showed three new bands at 952, 873 and 795  $\text{cm}^{-1}$  in addition to the AFBNP vibrations. Also, the IR spectrum for PWV-AFBNP (Figure 1c) showed three new bands at 966, 885 and 798  $\text{cm}^{-1}$  in addition to the AFBNP vibrations. These new bands were assigned to the stretching vibrations of terminal M=O, bridged corner shared, M-O<sub>b</sub>-M, and bridged edge shared, M-O<sub>c</sub>-M, octahedrons of the supported HPA, respectively [2,7,9,21]. The P-O stretching vibration of the supported HPA at around 1070  $\text{cm}^{-1}$  was covered by strong band of BNP Al-O vibration in this region (Figs. 1b and 1c).

These results confirmed that in one hand, the HPA are successfully supported on AFBNP and on the other hand, the structures of AFBNP and HPA did not change during



**Fig. 3.** Thermal analysis diagrams of a) PMoV-AFBNP and b) PWV-AFBNP.

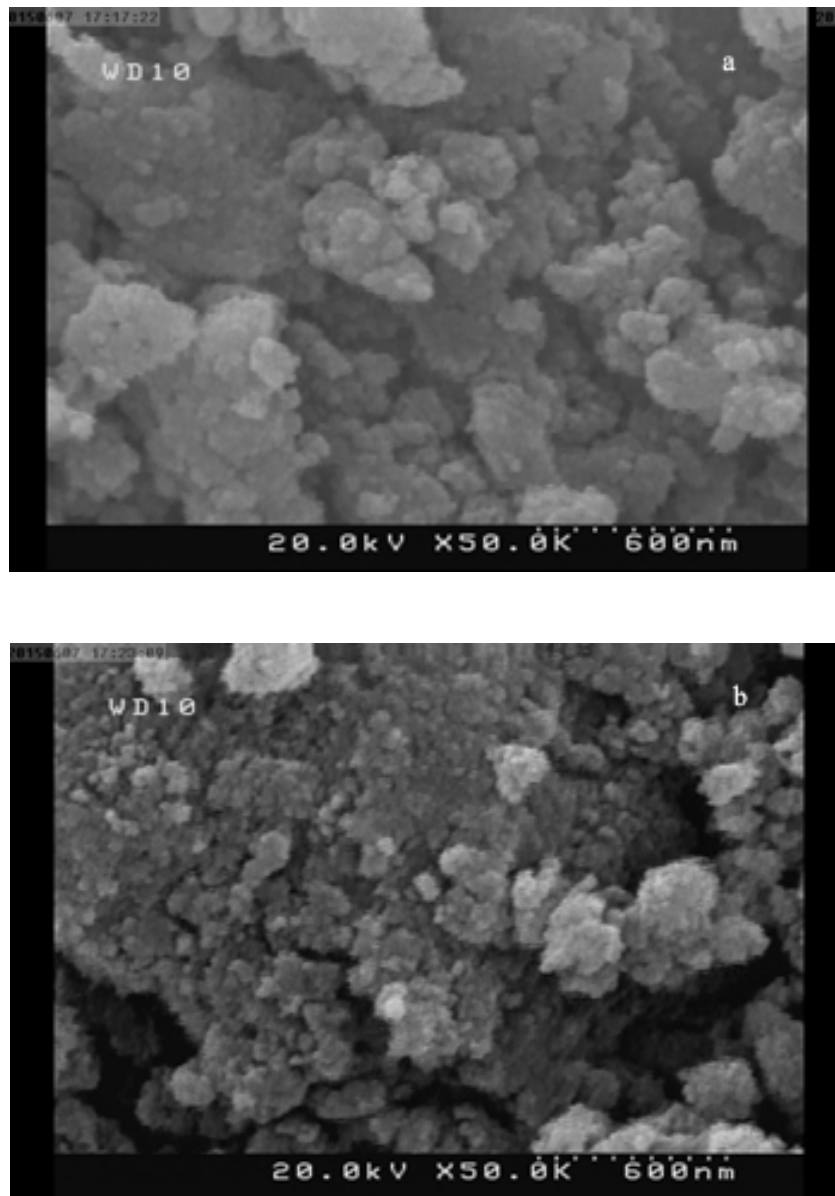
supporting processes.

Elemental analysis showed that the nitrogen content of AFBNP was 0.46%, which means that 0.33 mmol of the pending amine groups was covalently bonded to the surface of 1.00 g of BNP. The ICP analysis showed that approximately 96 and 93% of the nitrogen sites on AFBNP were used to electrostatic anchoring 0.32 and 0.31 mmol of the different HPA on 1.00 g PMoV-AFBNP and PWV-AFBNP, respectively.

The PXRD pattern for BNP was shown in Fig. 2. PXRD

patterns for AFBNP, PMoV-AFBNP and PWV-AFBNP were completely the same as BNP. These are confirmed that covalent bonding of amine functional groups and supporting of HPAs on them did not disturb the structure of BNP; and also showed that both HPAs were uniformly dispersed and not accumulated or crystallized onto the surface of AFBNP; otherwise they could show their crystalline structure in the diffraction patterns.

In the TG curve for PMoV-AFBNP (Fig. 3a), there is 10% weight loss below 100 °C which accompanied by a



**Fig. 4.** SEM images of a) PMoV-AFBNP and b) PWV-AFBNP.

peak in the DTG curve and could be attributed to the elimination of the physically-adsorbed water. The next weight loss in the TG curve is about 10% at around 450 °C which accompanied by a peak in DTG curve and may be attributed to the dehydroxylation of boehmite and crystallization of  $\gamma$ -alumina. The same feature with 8 and 18% weight losses were also observed in the TG/DTG curve of PWV-AFBNP (Fig. 3b).

Figure 4 shows the scanning electron microscopy (SEM) images of PMoV-AFBNP and PWV-AFBNP which both contains agglomerated particles.

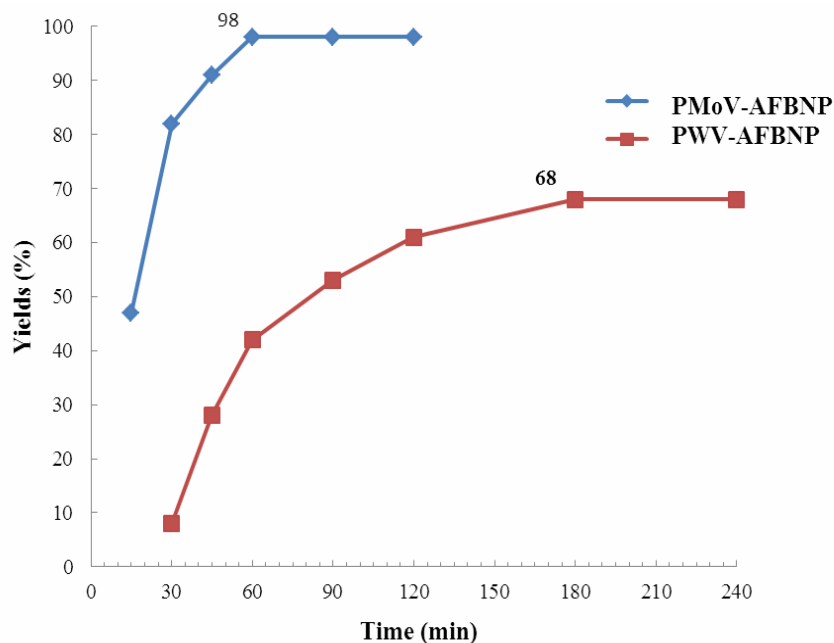
#### **Alkene Epoxidation with TBHP Catalyzed by HPA Supported on AFBNP**

Epoxidation of cyclooctene has been widely used as a model reaction to demonstrate the catalytic activity of the

**Table 1.** Epoxidation of *Cis*-cycloocten with TBHP under Reflux Conditions

Entry	Catalyst (mg)	Solvent (mL)	Catalyst loading (mol%) <sup>a</sup>	Oxidant/Substrate molar ratio	Time of reaction (min)	Epoxide yield (%) <sup>b</sup>
1	PMoV-AFBNP (20)	CH <sub>3</sub> CN (2)	1.28	2	60	No reaction
2	PMoV-AFBNP (20)	CH <sub>3</sub> OH (2)	1.28	2	60	No reaction
3	PMoV-AFBNP (20)	CH <sub>2</sub> Cl <sub>2</sub> (2)	1.28	2	60	37
4	PMoV-AFBNP (20)	CHCl <sub>3</sub> (2)	1.28	2	60	68
5	PMoV-AFBNP (20)	CCl <sub>4</sub> (2)	1.28	2	60	94
6	PMoV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.28	2	60	98
7	PMoV-AFBNP (5)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	0.32	2	60	21
8	PMoV-AFBNP (10)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	0.64	2	60	43
9	PMoV-AFBNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	0.96	2	60	69
10	PMoV-AFBNP (25)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.60	2	60	98
11	PMoV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.28	0.5	60	33
12	PMoV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.28	1	60	48
13	PMoV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.28	1.5	60	63
14	PWV-AFBNP (20)	CH <sub>3</sub> CN (2)	1.24	2	180	No reaction
15	PWV-AFBNP (20)	CH <sub>3</sub> OH (2)	1.24	2	180	No reaction
16	PWV-AFBNP (20)	CH <sub>2</sub> Cl <sub>2</sub> (2)	1.24	2	180	27
17	PWV-AFBNP (20)	CHCl <sub>3</sub> (2)	1.24	2	180	48
18	PWV-AFBNP (20)	CCl <sub>4</sub> (2)	1.24	2	180	65
19	PWV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.24	2	180	68
20	PWV-AFBNP (5)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	0.31	2	180	20
21	PWV-AFBNP (10)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	0.62	2	180	32
22	PWV-AFBNP (15)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	0.93	2	180	48
23	PWV-AFBNP (25)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.55	2	180	68
24	PWV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.24	0.5	180	15
25	PWV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.24	1	180	28
26	PWV-AFBNP (20)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (2)	1.24	1.5	180	41

<sup>a</sup>Calculated for 0.5 mmol cycloocten. <sup>b</sup>GLC yields are based on the starting cycloocten.



**Fig. 5.** Epoxidation of 0.5 mmol of *cis*-cyclooctene with 1.0 mmol of TBHP catalyzed by 20 mg of PMoV-AFBNP or PWV-AFBNP in 2 mL of  $C_2H_4Cl_2$  under reflux conditions.

new synthesized catalysts. It was chosen since cyclooctene epoxide is the only product of this reaction and it does not have any other byproduct. Thus we used this reaction to show and optimize the catalytic activity of these catalysts. The optimization of the title reaction was investigated by changing different parameters including the solvent, oxidant and catalyst. Our experiments showed that in the presence of these catalysts, *tert*-butylhydroperoxide (TBHP) is the only oxidizing system that can proceed the epoxidation of *cis*-cyclooctene in  $C_2H_4Cl_2$  and other oxygen sources such as hydrogen peroxide and sodium periodate (in the presence of 0.01 g of tetrabutylphosphonium bromide as the phase-transfer reagent), and urea-hydrogen peroxide in  $C_2H_4Cl_2$  or  $CH_3CN$  does not show an acceptable activity. It seems that the protic solvents, which were inevitably present with those oxidants, competed to bind to the metal centers and blocked the catalytic sites. Furthermore, under mild conditions, the epoxidation of *cis*-cyclooctene by TBHP did not proceed in the absence of the catalyst, as pointed out above. The detailed reaction conditions and obtained results are summarized in Table 1.

Studying the solvent effect in Table 1 (entries 1-6 and

14-19) showed the same trend as the other literature reports on homogeneous alkene epoxidation [22]. Coordinating solvents such as  $CH_3CN$  and  $CH_3OH$  compete with TBHP to occupy the coordination sites on the transition metal catalyst. Therefore, in the presence of these solvents, the observed yields are very low. Among other solvents, 1,2-dichloroethane has the highest yield of epoxide product for both catalysts. This could be attributed to the higher boiling point of  $C_2H_4Cl_2$  in comparison to the other solvents.

As another parameter, the amount of catalyst was investigated in the epoxidation of *cis*-cyclooctene with TBHP. Table 1 (entries 6-10 and 19-23) confirm that increasing the amount of the both catalyst up to 20 mg increased the cyclooctene epoxide yield.

The oxidant to substrate ratio is one of the most crucial parameters in the catalytic epoxidation processes. The results tabulated in Table 1 (entries 6, 11-13 and 19, 24-26) show that the optimum oxidant to substrate ratio was 2 and decreasing this ratio down to 0.5 for both catalysts, lowered the yields intensely.

Figure 5 shows the effect of reaction time on the epoxidation of *cis*-cyclooctene with TBHP. It reveals



**Table 2.** Epoxidation of some Alkenes with TBHP Catalyzed by PMoV-AFBNP and PWV-AFBNP under Reflux Conditions

Entry	Alkene	PMoV-AFBNP catalyst <sup>a</sup>			PWV-AFBNP catalyst <sup>a</sup>		
		Conversion (%) <sup>b</sup>	Epoxide (%) <sup>b</sup>	Time (min)	Conversion (%) <sup>b</sup>	Epoxide (%) <sup>b</sup>	Time (min)
1	Cycloocten	98	98	60	68	68	180
2	Cyclohexene	91	82 <sup>c</sup>	60	63	55 <sup>c</sup>	180
3	1-Octene	62	62	120	38	38	360
4	1-Hexene	52	52	120	29	29	360
5	Styrene	72	65 <sup>d</sup>	120	45	36 <sup>d</sup>	360
6	$\alpha$ -Methyl styrene	88	78 <sup>e</sup>	120	58	52 <sup>e</sup>	360
7	$\alpha$ -Pinene	81	81	120	52	52	360

<sup>a</sup>GLC yield based on the starting alkenes. <sup>b</sup>Reaction conditions: alkene (0.5 mmol), TBHP (1.0 mmol), catalyst (20 mg), C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (2 mL). <sup>c</sup>The byproduct (cyclohexanone) is 9% for PMoV-AFBNP and 8% for PWV-AFBNP.

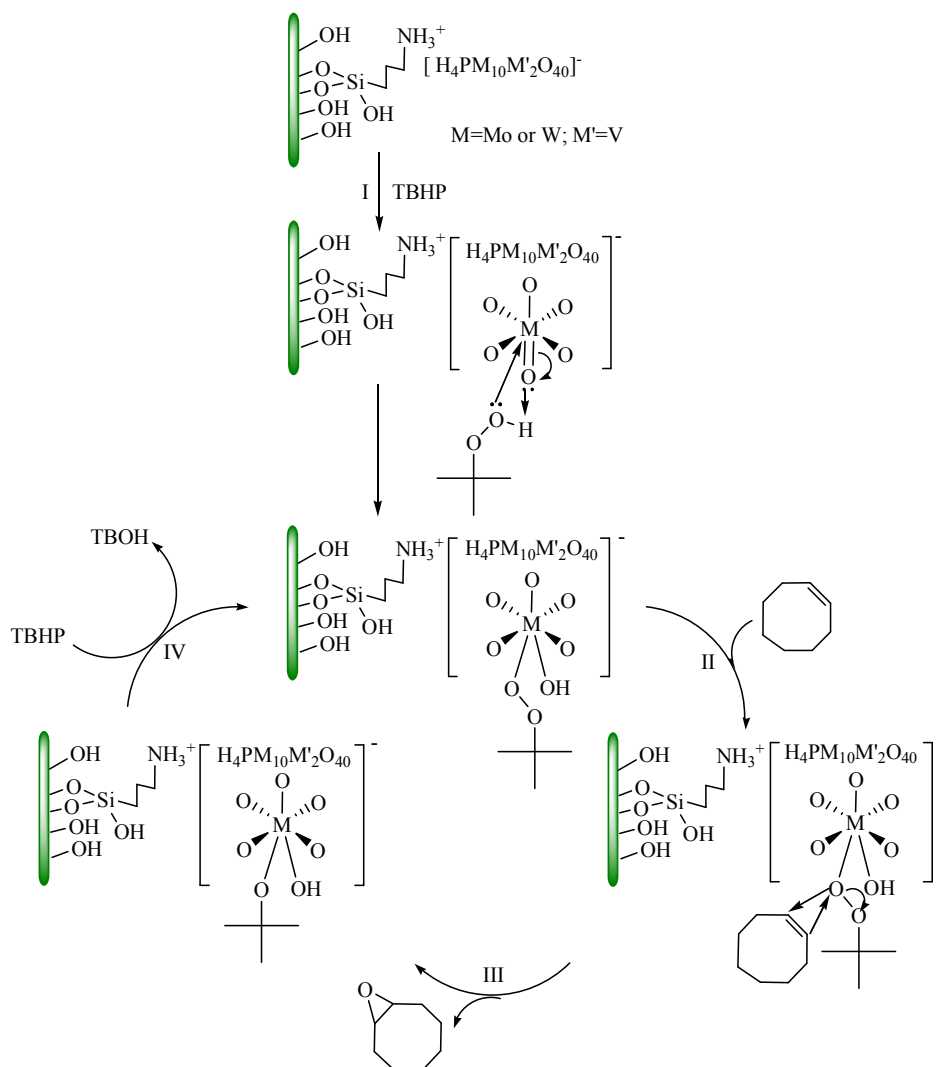
<sup>d</sup>The byproduct (benzaldehyde) is 7% for PMoV-AFBNP and 9% for PWV-AFBNP. <sup>e</sup>The byproduct (acetophenone) is 10% for PMoV-AFBNP and 6% for PWV-AFBNP.

that the PMoV-AFBNP catalyst is more reactive than PWV-AFBNP, and after 60 min, its conversion reaches a maximum, and then becomes constant. This could be attributed to the presence of Mo along with V in PMoV-AFBNP catalyst. By replacing Mo with W in PWV-AFBNP catalyst, the yield decreased and do not goes over 68% even after 4 h reflux.

Moreover, the heterogenic character of these catalysts was checked by the hot filtration test. For this purpose, each catalyst was removed by centrifuging the catalytic mixture in the middle of the optimization process, and the procedure was continued to reach an optimum time of reaction completion. The results obtained showed that when the catalyst was removed from the reaction medium, the catalytic procedure stopped and did not continue anymore.

This test proves that the catalytic reactions are held in heterogeneous conditions, and the catalysts are not leached to the reaction medium.

The new catalysts PMoV-AFBNP and PWV-AFBNP can also be used for the epoxidation of a wide range of substituted alkenes (Table 2). The blank experiments, performed without catalysts, with BNP or AFBNP, showed a very low conversion even after 5 h reflux but in the presence of both catalysts, a wide range of cyclic and linear alkenes could efficiently and selectively be converted to epoxides. Based on the epoxidation mechanisms suggested earlier [14-16] the higher electron-donating ability of an alkene double bond is expected to show a more epoxidation reactivity. Therefore, cyclooctene and cyclohexene with inner double bonds should exhibit more activities in



Scheme 2. Proposed mechanism for epoxidation of alkenes with TBHP by HPA supported AFBNP

comparison with 1-hexene and 1-octene that contain terminal double bonds. In addition, cyclooctene is more reactive than cyclohexene due to some cyclooctene conformations that favor the formation of reaction intermediates that decrease the activation energy [23]. In contrast, 1-octene is oxidized slower than 1-hexene, and this observation could be attributed to the more steric hindrance of the hexyl group connected to the double bond present in 1-octene in comparison with the butyl group in 1-hexene. A larger hexyl group can effectively hinder 1-octene in approaching the catalyst metal center, and slows down the

reaction.

Based on the experimental and theoretical reports [24], probable mechanisms were proposed for the epoxidation of cyclooctene with TBHP by the both catalysts (Scheme 2). According to our experimental results, the reaction rates depend on the catalyst and substrate concentrations. There are also some crucial stages in these processes. The first step for both catalysts involves the transfer of the TBHP hydroxyl proton to a terminal oxygen atom of these HPA complexes, which results in the coordination of the *tert*-butylperoxide anion to the Lewis acidic metal centers. Then

**Table 3.** Epoxidation of *Cis*-cycloocten with TBHP under Reflux Conditions Using Recycled Catalysts

Number of cycles	PMoV-AFBNP catalyst <sup>a</sup>				PWV-AFBNP catalyst <sup>a</sup>			
	Epoxide yield (%) <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>	PMoV <sup>d</sup>		Epoxide yield (%) <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>	PWV <sup>d</sup>	
			Leached (%) <sup>e</sup>	Content (mmol g <sup>-1</sup> ) <sup>f</sup>			Leached (%) <sup>e</sup>	Content (mmol g <sup>-1</sup> ) <sup>f</sup>
0	98	77	ND	0.32	68	55	ND	0.31
1	95	74	ND	0.32	65	52	ND	0.30
2	93	73	ND	0.31	61	49	ND	0.29
3	90	70	ND	0.30	55	44	ND	0.27
4	85	66	ND	0.28	48	39	ND	0.25

<sup>a</sup>Reaction conditions: 0.5 mmol cycloocten, 1.0 mmol TBHP, 20 mg catalyst, 2 mL C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, 60 min for PMoV and 180 min for PWV. <sup>b</sup>GLC yields are based on the starting cycloocten. <sup>c</sup>TOF = (mole of reactant) (yield/100)/(mole of catalyst) (time). <sup>d</sup>Determined by ICP analysis. ND: not detected. <sup>e</sup>HPA leached from catalyst into the catalytic solution medium. <sup>f</sup>HPA content of recycled catalyst.

the alkene substrate is coordinated to the metal center, and, as a nucleophile, is inserted into the metal oxygen bond of the coordinated peroxide electrophile anion. This mechanism easily explains the faster reaction of the electron-rich alkenes in comparison to the electron-poor ones. In the next step, the epoxide product is formed, and the *tert*-butylperoxide anion is converted to the *tert*-butoxide anion. Then the peroxide product is released and the catalytic cycle is continued by substitution of a new *tert*-butylperoxide instead of the *tert*-butoxide anion.

### Catalyst Recovery and Reuse

As discussed earlier, the reusability of the solid-supported catalysts is one of their most important benefits. Therefore, reusability of the both new HPA supported catalysts were monitored by means of the multiple sequential epoxidation of *cis*-cycloocten with TBHP (Table 3). After each cycle, the reaction mixture was centrifuged, and the supernatant solutions and recovered catalysts were analyzed by means of ICP. This analysis showed that there was no metal contaminant in the supernatant solution, but there are some sensible decreases

in the metal loading of the recovered catalysts. This could evidence that why the recovered catalysts after four cycles lose 13-20% of their activity in the epoxidation of cyclooctene.

TOF is an honest parameter for the comparison of the catalytic activities, so we used it to show the benefits of our catalytic systems over the other reported catalytic protocols. Mahjoub *et al.* have supported H<sub>3</sub>PM<sub>12</sub>O<sub>40</sub>.n[(((CH<sub>3</sub>)<sub>2</sub>N)<sub>3</sub>PO)] (M = W or Mo) complex onto SBA-15 and reached TOF of ~20-30 h<sup>-1</sup> in the epoxidation of *cis*-cyclooctene with H<sub>2</sub>O<sub>2</sub> [8]. Very recently, Feng *et al.* have supported a dioxo-molybdenum complex onto an organic copolymer and reached a TOF of 5 h<sup>-1</sup> in the epoxidation of *cis*-cycloocten with TBHP [25]. Moahmmadikish *et al.* have supported a molybdenum complex onto nanomagnetite, and reported a TOF of 19 h<sup>-1</sup> with the same catalytic reaction conditions [26]. Yang *et al.* have also supported a molybdenum Schiff base complex onto SBA-15 and reached a TOF of 25 h<sup>-1</sup> in the same reaction [27]. All of these reports have lower TOF values than both of this research catalysts (~77 h<sup>-1</sup> for PMoV-AFBNP and ~55 h<sup>-1</sup> for PWV-AFBNP).

## CONCLUSIONS

We successfully prepared new hybrid heterogeneous catalysts by anchoring Keggin type HPA of  $H_5[PMo_{10}V_2O_{40}]$  and  $H_5[PW_{10}V_2O_{40}]$  onto the surface of AFBNP. These are active catalysts for the epoxidation of various alkenes under heterogeneous conditions.

Many molybdenum complexes have been reported for the catalytic epoxidation of alkenes with TBHP. However, PMoV-AFBNP catalytic system is superior to most of them in terms of cost, reaction time, selectivity, conversion and turn-over frequency (TOF).

There are some crucial factors that considerably change the yields. Among them, the type of solvent is the most predominant, and  $C_2H_4Cl_2$  as an aprotic, non-polar and hydrophobic solvent gave the best results.

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