Heterogenized molybdovanadophosphoric acid on amine-functionalized SBA-15 for selective oxidation of alkenes

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Mono-vanadium substituted molybdovanadophosphoric acid has been immobilized on amine-functionalized SBA-15 and characterized by different techniques. Small angle X-ray scattering (SAXS) analysis and SEM technique provide evidence for the structural integrity of the amine-functionalized SBA-15 and for the molybdovanadophosphoric acid immobilized sample. Diffuse reflectance UV–vis, ^{31}P, ^{51}V-NMR and FT-IR data confirm the incorporation of molybdovanadophosphoric acid onto the amine-functionalized SBA-15. The textural properties of these materials were studied by nitrogen sorption studies. Oxidation of selected substrates, norbornene, cyclooctene, cyclohexene and styrene with aqueous hydrogen peroxide was carried out with the immobilized molybdovanadophosphoric acid catalyst (heterogenized) and the results were compared with that of the neat molybdovanadophosphoric acid catalyst (homogeneous). The selectivity of the desired products was higher with the immobilized catalyst. The immobilized catalyst could be separated after the reaction and the reusability of the catalyst has also been demonstrated.

KEY WORDS: SBA-15, amine-functionalized SBA, mesoporous material, heteropolyacid, molybdovanadophosphoric acid, catalyst characterization (XRD, ^{31}P -NMR, diffuse reflectance UV–vis, SEM).

1. Introduction

Heterogenization of homogeneous catalytic materials has been an attractive strategy to overcome the difficulties involved in the separation and reusability of homogeneous catalysts [1,2]. Many strategies have been adopted in the literature to heterogenize the homogeneous catalysts. Conventionally they are immobilized/anchored on polymeric organic materials such as resins [3,4], supported on inert porous solids such as alumina and silica [5,6] or encapsulated in the pores and cavities of microporous and mesoporous materials such as zeolites, MCM-41 and SBA-15 [7–9]. There are certain disadvantages with polymeric supports due to their vulnerability of their organic part to some chemicals and solvents, and due to leaching of catalysts from the immobilized material over the period of reactions [10]. On the other hand, porous inorganic material supports are structurally stable and more resistant to organic chemicals and solvents. However, mere encapsulation of the homogeneous catalytic molecules into the porous materials also leads to partial leaching of catalysts. Moreover, controlling the amount of loading of catalytic molecule is limited when encapsulation technique is adopted [11].

To overcome the leaching problem, efforts have been made to immobilize the catalytic molecules on a functionalized silica surface, for example, microporous and mesoporous materials with organic chain containing terminal functional groups like amine, phosphine, sulfide, etc. [2]. Anchoring of the homogeneous catalysts onto these functionalized materials is proven to be effective in reducing the leaching problem. These inorganic materials are more versatile than polymeric supports as pore dimensions, specific surface area and mesoporous structure of them can be controlled to a large extend. A great deal of research work has been done on X- and Y-type zeolites and M41 based mesoporous materials. Amongst mesoporous materials, SBA type support materials are more attractive due to their better hydrothermal stability, large pores and thick walls.

Transition metal ion substituted heteropoly compounds are, in general, promising catalysts for many catalytic applications including selective oxidation reactions [12]. High solubility of these molecules often makes their separation from the reaction mixture difficult. Heterogenizing these homogeneous molecules by immobilizing on mesoporous materials (e.g. MCM-41, SBA-15) were successful and found to be stable and active [13–16]. It was found that the encapsulation technique enhanced easy separation of these heteropoly anions from the reaction mixture; however, weak bonding interaction of heteropoly anion with the silanol group of these silicate materials leads to partial leaching especially with polar solvent media [17,18]. In the recent literature, anchoring of homogeneous catalyst molecules onto amine functionalized silica materials like propyl amine-functionalized mesoporous materials was found to be a promising strategy to reduce the leaching of active sites [18–20].

In the present paper, we report anchoring of mono-vanadium substituted phosphomolybdic acid on amine-

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functionalized SBA-15 and their physicochemical characterization. Catalytic reactions have been carried out to demonstrate the heterogeneous nature and reusability of the immobilized catalyst.

2. Experimental

2.1. Materials

All chemicals used are of analytical reagent grade. Disodium hydrogen phosphate dodecahydrate, sodium molybdate dihydrate and sodium meta vanadate (Loba Chemicals), conc. H_2SO_4 were used as received for the preparation of vanadium substituted phosphomolybdic acid. Aq. H_2O_2 (30%) was purchased from Merck. Diethyl ether and acetonitrile (s.d. fine) were of analytical grade and used without further purification. The exact strength of hydrogen peroxide was determined by redox titration with $KMnO_4$ solution. Tetraethyl orthosilicate (TEOS), (3-aminopropyl)-triethoxysilane (APTES), and the triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) [EO_{20}-PO_{70}-EO_{20}) were used as received (Aldrich). Hydrochloric acid (2 M) was prepared from 37% fuming hydrochloric acid (Merck). The substrates norbornene, cyclooctene, cyclohexene and styrene were purchased from Aldrich chemical Co. and were used without further purification.

2.2. Synthesis of SBA-15

SBA-15 was prepared by known method as described elsewhere [21]. Typically, 4 g of triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) [EO_{20}-PO_{70}-EO_{20}, a template], was dispersed in 30 g distilled water and stirred for 3 h. To the resultant solution, 120 g of 2 M HCl was added under stirring and finally 8.5 g of tetraethyl orthosilicate (TEOS, a silicate precursor) was added drop wise. The resultant mixture was maintained at 40 °C for 24 h under stirring and then at 110 °C for 48 h under static condition in a Teflon bottle. The crystallized product was filtered, washed with warm distilled water and dried at 110 °C for 24 h. The dried sample was then calcined at 550 °C at 1 °C/min rate and holding it at 550 °C for 6 h. The structure was confirmed by small angle X-ray scattering (SAXS) analysis. The surface area was determined by N_2 BET measurement at liquid nitrogen temperature. The calcined sample is referred as SBA here after.

2.3. Preparation of amino-functionalized SBA-15

The surface modification of SBA using (3-aminopropyl)triethoxysilane (APTES), was carried out using a grafting method by adopting reported procedure [21]. In a typical preparation freshly activated SBA-15 (2 g) was refluxed with 50 mL of toluene (distilled over sodium and dried) to remove the occluded moisture azeotropically for 4 h. To that APTES (1 g) in 10 mL of toluene was added with stirring and refluxed for 4 h. After distilling off the solvent, the solid was filtered, washed in a soxhlet apparatus with dichloromethane, and then dried at room temperature. The product is designated as NH_2–SBA. The nitrogen elemental analysis estimated 2.3 mmol of NH_2 per gram of NH_2–SBA.

2.4. Preparation of molybdovanadophosphoric acid

Molybdovanadophosphoric acid, $H_4PMo_{11}VO_{40}$ (VHPA), was prepared by adopting the reported procedure [22]. A typical procedure involves mixing of appropriate amounts of acidified aqueous solution of Na_2HPO_4 and $NaVO_3$ with a solution of Na_2MoO_4. The products were then separated as their respective etherates by extracting with diethyl ether. A stream of air was passed through the heteropolyetherates to remove the ether. The orange powder thus obtained was recrystallized from water. The crystals were air dried and stored over conc. H_2SO_4 in a desiccator. The molybdovanadophosphoric acid was characterized by IR, UV–vis, NMR techniques and elemental analysis. Number of water molecules was found to be 18 as estimated from TGA measurement. ^{31}P NMR (δ, CH_3CN at 23 °C):−1.46 ppm, ^{51}V NMR (δ, CH_3CN at 23 °C):−540.1 ppm.

2.5. Anchoring of molybdovanadophosphoric acid onto NH_2–SBA

Freshly activated NH_2–SBA (0.9 g) was added 50 mL of acetonitrile solution containing 0.1 g of molybdovanadophosphoric acid (VHPA) and refluxed for 3 h. The sample was then filtered, washed, and soxhleted using acetonitrile solvent for 12 h and dried at 100 °C under vacuum. The final materials are designated as NH_2–SBA–VHPA. The nitrogen elemental analysis estimated 2.1 mmol of NH_2 per gram of NH_2–SBA–VHPA. Vanadium content estimated by ICP-OES and was 0.24 ppm.

2.6. Characterization

SAXS pattern of the samples was obtained in reflection mode using a Rigaku Dmax 2500 diffractometer and Ni filtered copper radiation. The samples were scanned in the range $2\theta = 0.5$–$6°$ and the generator was operated at 40 kV and 150 mA. Nitrogen adsorption measurements were measured on a NOVA 1200 (Quantachrome) at 77 K. First the samples were activated at 453 K for 3 h under vacuum and then the adsorption–desorption was conducted by passing N_2 into the sample, which was kept under liquid nitrogen. The specific surface area of the samples were calculated using the multiple-point Brunauer–Emmett–Teller (BET) method in the relative pressure range *P*/

P_0 = 0.05–0.3. The pore size distribution curves were computed by using the Barrett–Joyner–Halenda (BJH) method. The pore sizes were obtained from the peak positions of the distribution curves. The elemental analysis (C and N) was carried out with an EA1108 Elemental Analyser (Carlo Erba Instruments). V and Mo contents were estimated by ICP (Perkin Elmer Plasma 1000 Emission Spectrometer). The FT-IR spectra for the powdered samples were obtained over a range of 400–4000 cm^{-1} on a Shimadzu FT-IR 8201 PC and the spectra were recorded as a mull in fluorolube for the region 4000–1350 cm^{-1} and as a nujol mull for 1350–400 cm^{-1} range. Diffuse reflectance UV–vis spectra were recorded on a Shimadzu UV–vis spectrophotometer (UV-2500 PC) using barium sulfate as the standard. High-resolution NMR studies were carried out on a Bruker DRX-500 MHz spectrometer. ^{31}P NMR chemical shifts were referenced to external phosphoric acid and ^{51}V chemical shifts were referenced to $VOCl_3$. SEM pictures of the samples were recorded on a JEOL-JSM-5200 scanning electron microscope with a resolution of 5.5 nm.

2.7. *Catalytic activity*

All the reactions were carried out in a glass reactor at 60 °C in acetonitrile solvent. Typically 0.01 mol of substrate and 0.01 mol of aqueous hydrogen peroxide (30%) were taken in 10 mL of solvent and 10 mg (5 μmol) of VHPA catalyst was added. The reaction mixture was stirred constantly at the required temperature and was subjected to GC analysis (SPB™ −5, 30 m ×,0.53 mm, 3.0 μm film thickness Supelco fused silica capillary column, N_2, FID, internal standard-chlorobenzene) periodically to monitor the conversion of the substrate and selectivity of the products. In the case of the immobilized sample, amount of catalyst containing 5 μmol of V content was taken for the reaction. After the reactions, the immobilized catalyst was removed by careful filtration, washed with acetonitrile dried in air, and then reused.

3. Results and discussion

3.1. *Synthesis and characterization*

Schematic representation of amine functionalization of SBA-15 and subsequent immobilization of molybdovanadophosphoric acid on the functionalized material is given in figure 1. Vanadium substituted heteropolyacid sample was orange in color and the color becomes light during the immobilization with NH_2–SBA. The combined filtrate after washing and soxhleting was subjected to UV–vis analysis and found no characteristic bands for molybdovanadophosphoric acid that possibility indicates retention of all the VHPA in the pores of NH_2–SBA. The ICP analysis of immobilized sample supports the above observation.

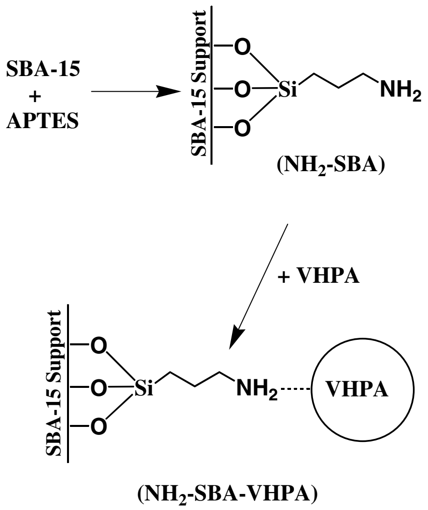


Figure 1. Schematic representation of functionalization of SBA-15 and subsequent heterogenization of molybdovanadophosphoric acid (VHPA) on amine-functionalized SBA-15.

SAXS patterns for SBA, NH_2–SBA and NH_2–SBA–VHPA are depicted in figure 2. Three reflections, one strong reflection at (100) and two with low intensity at (110) and (200) planes, are seen in the range 2θ = 0.9–2 °for all the samples, indicating a significant degree of long-range ordering in the structure and well-formed hexagonal pore arrays. The d_{100} positions are similar for all the samples that probably indicate the structural ordering of SBA is not affected upon modification with APTES and on anchoring with VHPA. However, comparing with pure SBA and NH_2–SBA small reduction in intensity of reflection (100) was noticed on

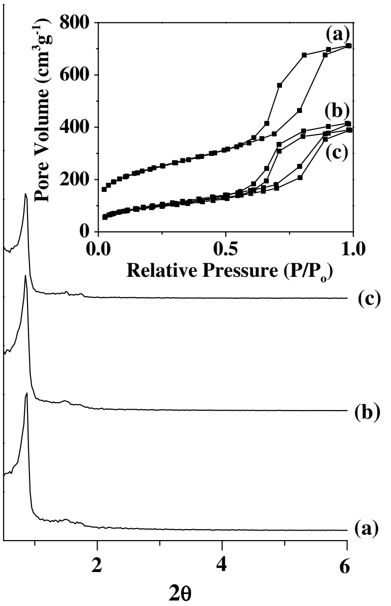


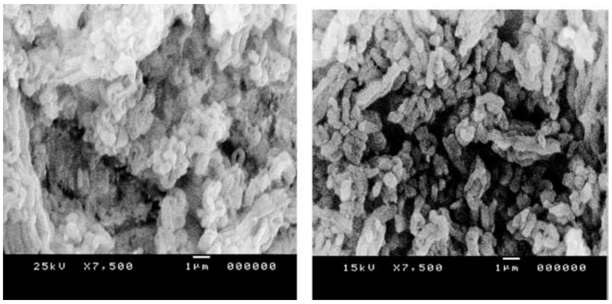
Figure 2. SAXS patterns of (A) SBA-15 (B) NH_2–SBA and (C) NH_2–SBA–VHPA. (inset: nitrogen sorption isotherms of these samples).

Table 1
Structural properties of SBA, NH_2–SBA and NH_2–SBA–VHPA samples characterized by N_2 adsorption

Samples	S_{BET}(m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (BJH) (nm)
SBA	859	1.1	8.9
NH_2–SBA	360	0.64	7.13
NH_2–SBA–VHPA	347	0.60	6.89

immobilizing the VHPA onto NH_2–SBA. This observation indicates anchoring of molybdovanadophosphoric acid was indeed occurred inside the pores of SBA [20, 23].

The nitrogen sorption isotherms for all the samples were carried out by BET method at 77 K and are depicted in figure 2 (inset). The parameters calculated from nitrogen adsorption data using the BJH method are listed in table 1. The samples display a type IV isotherm with H1 hysteresis and a sharp increase in volume adsorbed above $P/P_0 \sim 0.7$ which is characteristic of highly ordered mesoporous materials. The textural properties of SBA substantially maintained over amine functionalization and on subsequent anchoring of VHPA [23,24]. Surface area of SBA has reduced from 859 to 360 m^2/g on amine functionalization and it was further reduced to 347 m^2 /g upon anchoring the VHPA. Similarly there was a reduction in pore volume on functionalization and on loading of VHPA compared with that of the pure SBA sample. These observations indirectly confirm the anchoring of VHPA onto NH_2–SBA. The reduction in surface area and pore volume might be due to the covering and/or filling of pores by bulkier trisiloxypropyl amine group and the heteropolyacid anion. The BHJ pore size distribution curves derived from the desorption isotherm were similar for all the samples. The observation of similar pore size distribution for all the samples again indicates the integrity of ordered pore structure. The SEM images of SBA, NH_2–SBA and NH_2–SBA–VHPA samples are shown in figure 3 and the images are similar to the reported literature on SBA and amine-functionalized SBA samples [25–27]. The images of all the samples show hexagonal particles organized into rope-like structures, which are further agglomerated into elongated particles.



(i) NH_2-SBA (ii) NH_2-SBA-VHPA

Figure 3. SEM images of pure NH_2–SBA and NH_2–SBA–VHPA.

3.2. Spectroscopy studies

Anchoring of VHPA on the amine-functionalized SBA were investigated by different spectroscopic tools. The FT-IR study was performed to identify the presence of VHPA in NH_2–SBA–VHPA. FT-IR spectrum of NH_2–SBA–VHPA was compared with that of NH_2–SBA and pure VHPA [20]. NH_2–SBA shows two medium intensity bands at 3370 and 3299 cm^{-1} that are characteristic of the NH_2 group which are absent in VHPA (figure 4). In 400–1100 region, neat VHPA sample shows four peaks (1059, 958, 873, 722 cm^{-1}) characteristic of phosphomolybdic acid (figure 4(A)). Since most of the IR bands of pure NH_2–SBA sample (1059, 958, 800, 722, 458 cm^{-1}, figure 4(C)) overlaps with that of pure VHPA, the bands characteristics of heteropoly anion was not clearly seen in IR spectrum of NH_2–SBA–VHPA (figure 4(B)). However, increase in intensity of IR bands at 800, 958, and 1059 cm^{-1} and appearance of a new shoulder at 894 cm^{-1} in NH_2–SBA–VHPA with respect to that of NH_2–SBA (figure 4(B)) may be considered as an indication for the presence of VHPA in the pores of NH_2–SBA [13].

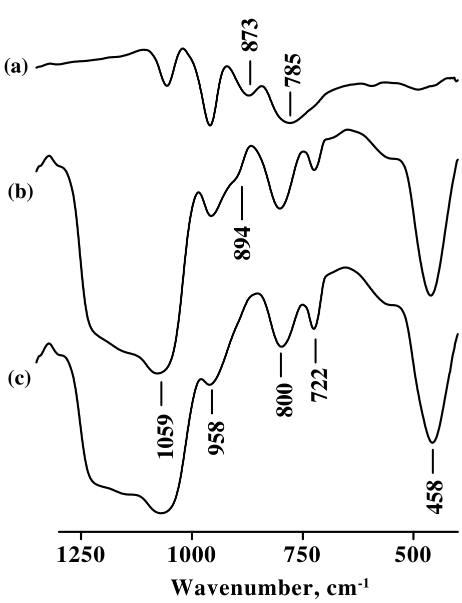


Figure 4. FT-IR spectra of (A) pure VHPA (B) NH_2–SBA–VHPA and (C) NH_2–SBA.

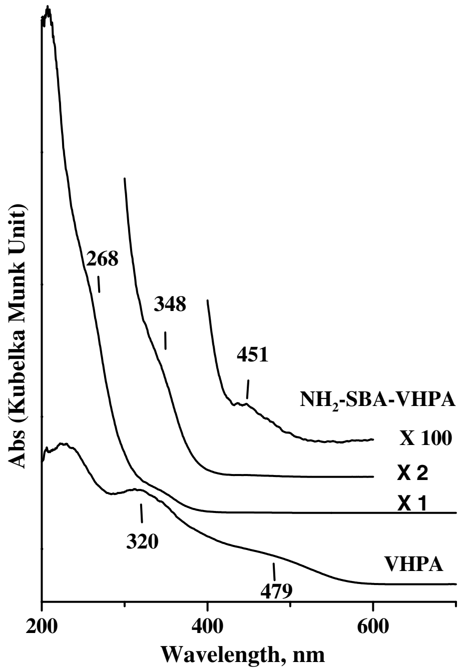


Figure 5. Diffuse reflectance UV–vis spectra of NH_2–SBA–VHPA and neat VHPA.

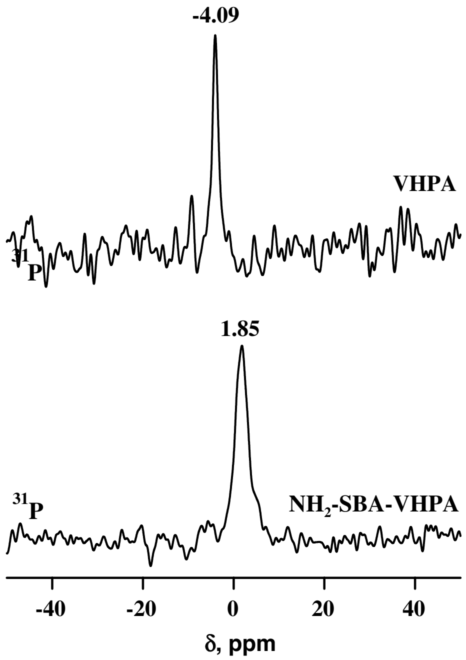


Figure 6. ^{31}P MAS NMR spectra of neat VHPA and NH_2–SBA–VHPA samples.

Molybdovanadophosphoric acid shows characteristic UV–vis bands and therefore their structures have often been characterized by diffuse reflectance UV–vis spectroscopy. There was no characteristic peaks for SBA and NH_2–SBA in 220–400 nm region; however, NH_2–SBA–VHPA exhibits certain features of metal to ligand charge transfer transitions. In figure 5, these bands are compared with that of the neat VHPA which exhibits characteristic bands around 229, 320 and 479 nm. However, upon immobilization of VHPA on NH_2–SBA these bands are slightly shifted and broad features are seen at 207, 268, 348 and 451 nm. Since some of these bands are weak due to low concentration of VHPA in the immobilized sample, they are shown in expanded scale for clarity. The presence of these bands indicates the occupation of VHPA in the pores of SBA sample and the small shifts in wavelength of these bands should be due to constraints around the heteropolyacid anion and/or due to its interaction with NH_2–SBA.

Additional evidence for the immobilization of VHPA on the amine-functionalized SBA was imparted by ^{31}P NMR spectral analysis. ^{31}P MAS NMR spectrum was recorded for NH_2–SBA–VHPA and compared with that of neat VHPA sample in figure 6. A ^{31}P signal was seen for the neat VHPA at −4.9 ppm and it was shifted to 1.85 ppm for NH_2–SBA–VHPA. Due to the extreme sensitivity of ^{31}P nucleus to its local environment, any slight changes in the chemical environment due to the interaction between the support and VHPA could have caused the difference. The difference in the chemical shift can also be due to the difference in degree of hydration of VHPA upon immobilization as it is known that ^{31}P NMR signal of the heteropolyacid anion is sensitive to degree of hydration [28–30]. Thus, the above spectral studies along with the small angle X-ray and surface studies clearly provide evidence for the presence of VHPA inside NH_2–SBA. A further detailed spectroscopic investigations are under progress to understand the exact nature of interaction between the amine-functionalized unit of NH_2–SBA and VHPA.

3.3. *Catalytic activity and catalyst recycling*

Molybdovanadophosphoric acid has been reported to be an active catalyst for the selective oxidation of several organic substrates with peroxides as oxidants [34,35]. In the present work, catalytic activity of NH_2–SBA–VHPA was examined for oxygenation of few representative substrates namely norbornene, cyclooctene, cyclohexene and styrene with aqueous hydrogen peroxide as an oxidant at 60 °C in acetonitrile solvent. The results were compared with that of the reaction with the neat VHPA (homogeneous catalyst) under identical experimental conditions (table 2). As shown in the table, the selectivity was always higher when the heterogeneous catalyst was used. For example, for the oxidation of norbornene the conversion was more than 70% with the neat VHPA but the selectivity of epoxynorbornene was only 58% and the other products were norborneol and norbornanone. However, with the NH_2–SBA–VHPA the selectivity for the epoxide was more than 99% though the conversion was lower. Similarly, oxidation of cyclooctene with the neat catalyst gave cyclooctene

Table 2
Oxidation of few representative alkenes with aqueous hydrogen peroxide using the neat (VHPA) and heterogenized (NH_2–SBA–VHPA) catalysts

No	Substrate	VHPA		NH_2–SBA–VHPA	
		Conv. mol %	Products (selectivity) mole %	Conv. mol %	Products (selectivity) mole %
1	Norbornene	70	Epoxynorbornane (58) Norborneol (17) Norbornanone (25)	26	Epoxynorbornane (>99)
2[a]	Norbornene	–	–	25	Epoxynorbornane (>99)
3[b]	Norbornene	–	–	24	Epoxynorbornane (>99)
4	Cyclooctene	30	Cyclooctene oxide (75) Cyclooctanol (13) Cyclooctanone (12)	23	Cyclooctene oxide (>99)
5	Cyclohexene	35	Cyclohexanol (34) Cyclohexanone (20) 2-Cyclohexene-1-ol (30) 2-Cyclohexene-1-one (16)	32	Cyclohexene oxide (23) 2-Cyclohexene-1-ol (67)
6	Styrene	24	Benzaldehyde (70) Phenylacetaldehyde (15) Benzoic acid (15)	12	Benzaldehyde (>99)

Reaction conditions: VHPA catalyst = 10 mg; NH_2–SBA–VHPA catalyst = 100 mg, substrate = 0.01 mol; aqueous H_2O_2 (30%) = 0.01 mol[a,b]First and twice recycled NH_2–SBA–VHPA catalyst respectively, temperature = 60 C, time, 3 h, solvent = acetonitrile.

oxide with only 75% selectivity at 30% conversion; however, with the NH_2–SBA–VHPA cyclooctene oxide was the only product. In case of cyclohexene the conversions with the neat and the immobilized catalysts were nearly equal; however, 2-cyclohexene-1-ol and cyclohexene oxide were the main products with the solid catalyst while the neat catalysts produced four products. With styrene, benzaldehyde was only product with the NH_2–SBA–VHPA unlike the neat VHPA catalyst which gave multiple products. The results are summarized in table 2. The reason for the multiple product formation with neat VHPA may be due the fast decomposition of H_2O_2 (as noticed by the effervescence soon after the addition of H_2O_2) which might have led to a high conversion of substrates and the formation of many kinetically stable products. Such an effervescence was absent in the case of NH_2–SBA–VHPA catalyst. Thus, the higher selectivity with the heterogenized catalyst can be attributed to slow decomposition of hydrogen peroxide which might have maximized the availability of oxo-species for the formation of selected products.

The reusability of the heterogenized catalyst was tested as follows:after 3 h of norbornene oxidation reaction, the NH_2–SBA–VHPA catalyst was filtered from the reaction mixture and washed with acetonitrile to remove the unreacted substrate and oxidant, and the products. The recovered catalyst was dried and used for the fresh reaction under identical experimental conditions. The cycle was repeated twice and the results are given in table 2 (entry number 2 and 3). It was found that the recycled catalyst was stable and active for many catalytic cycles but with a small reduction in the conversion; however, the selectivity remains very high (>99%). To check the leaching of vanadium and molybdenum ions from the immobilized catalyst, the filtrate after separating the catalyst at the end of the reaction were analyzed by ICP. Amount of Mo and V contents in the filtrate was 1.1% of total amount taken, indicating a small fraction of vanadium and molybdenum leached into the solution upon the interaction with the aqueous hydrogen peroxide oxidant.

To understand further the catalytic activity of the heterogenized catalyst versus the possible homogeneous reaction with the leached VHPA, the following experiment was carried out:the solid catalyst part was separated from the reaction mixture containing NH_2–SBA–VHPA, cyclooctene, aqueous H_2O_2 and acetonitrile by careful filtration after 2 h of reaction and the reaction was continued further with the remaining filtrate at the same experimental condition but with the fresh addition of H_2O_2. The kinetic profiles of the reaction with the heterogenized catalyst and that after filtering the same at 2 h of reaction time were compared in figure 7. In the case of former, the conversion continues steeply and steadily with time while in the latter case, it progressed only slightly (less than 2% after filtering the catalyst) and reached the steady state thereafter. The above result may probably indicate partial leaching of VHPA into the filtrate albeit it was small. To understand the amount of leached VHPA catalyst needed to have 2% conversion, the above reaction was carried out with varying amount of neat VHPA catalyst and it was found that less than 1% of total amount of VHPA taken (i.e. 1% of 10 mg) was

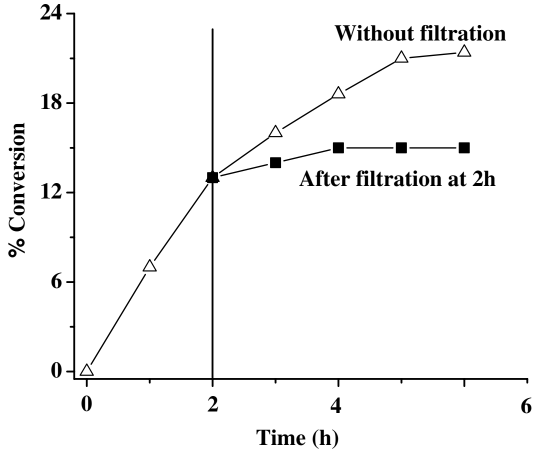


Figure 7. Reaction profile of epoxidation of cyclooctene with aqueous hydrogen peroxide in the presence of NH_2–SBA–VHPA (A) without filtration of the catalyst and (B) after filtration of the solid-catalyst at 2 h of reaction. The reaction condition:catalyst = 100 mg; cyclooctene = 0.01 mol; aqueous H_2O_2(30%) = 0.01 mol, temperature = 60 °C, solvent = acetonitrile.

needed for this slight increase in conversion with the filtrate after filtration of the immobilized catalyst. The results are consistent with the ICP analysis of the filtrate.

4. Conclusion

Mono-vanadium substituted molybdovanadophosphoric acid was immobilized on amine-functionalized SBA-15 and was characterized by different techniques. SAXS analysis provides evidence for the structural integrity of the amine-functionalized SBA even after immobilizing with molybdovanadophosphoric acid. The synthesized materials were also characterized by nitrogen sorption studies, UV–vis, NMR, and IR studies provided evidence for the presence of VHPA inside the NH_2–SBA. The catalytic activity of the immobilized sample (NH_2–SBA–VHPA) were studied for few substrates with aqueous hydrogen peroxide at 60 °C and compared with the neat VHPA catalyst. It was found that selectivity of the products are higher with the immobilized catalyst. The catalyst part can be separated after the reaction and can be reused for few cycles without losing its activity.

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