Influence of silica source in the catalytic activity and heterogenity of mesoporous vanadosilicates

S. Shylesh, S.P. Mirajkar, A.P. Singh *

Catalysis Division, National Chemical Laboratory, Pune 411008, India

Abstract

Vanadium-substituted ordered mesoporous silicates (V-OMS) were synthesized hydrothermally using two common silica sources, viz. fumed silica and tetraethyl orthosilicate, and their surface properties and catalytic activities were evaluated in the liquid phase oxidation of 1-napthol using aqueous H_2O_2 as an oxidant. The catalysts were characterized by XRD, N_2 adsorption–desorption, DRUV–vis and TPR to evaluate the mesostructural ordering and the local environment of vanadium in the MCM-41 matrix. Characterization data of the fresh calcined catalysts reveal a more ordered hexagonal structure for the V-MCM-41 catalyst prepared by using tetraethyl orthosilicate as the silica source while spent catalyst showed that the material is less stable than the V-MCM-41 catalyst prepared by using fumed silica as the silica source. Further, the observed differences in the selectivity behavior of extracted and calcined forms of both vanadium catalysts shows that the treatment conditions had a decisive role in the formation of extra framework metal species and further in the mesoscopic structural ordering.
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1. Introduction

Molecular sieves with transition metals incorporated into the framework had attracted great interest in catalytic oxidation process, especially for the production of fine chemicals [1–3]. Among them titanium and vanadium-containing zeolitic materials (TS-1 and VS-1) receive considerable attention as they show well isolated reactive sites and hence found to be active in a number of liquid phase oxidation reactions using H_2O_2 as oxidant. However, the inherent limitations in the number of metal ions per unit cell and small pore diameter restrict their application towards substrates having kinetic diameters above 7 Å and to the use of organic peroxides as oxidizing agent. On the other hand, the fascinating discovery of mesoporous M41S materials by Mobil researchers [4] in the early nineties, unravel the limitations of the microporous crystalline zeolites, as the mesoporous MCM-41 having large surface areas, variable pore diameters and high-density surface silanol sites provides incorporation of active redox metal ions by direct hydrothermal methods or by post-synthesis modifications in a quite simple way and are reported to catalyze the oxidation of bulkier aromatics using H_2O_2 or TBHP as oxidants.

Even though, literature shows several examples of highly active vanadium-containing mesoporous materials (V-MCM-41, V-MCM-48 and V-HMS), serious drawbacks of this procedure lies in the way that a large part of the incorporated active metal sites are well buried inside the pore channels and hence are unapproachable for the reactant molecules to initiate the reaction [5–9]. Furthermore, the inherent leaching problem of the extra framework species always confuses on the heterogenity of these mesoporous silicates. This limitation is largely attributed to the presence of thin pore walls, which may gets seriously damaged under strong oxidizing reaction conditions, thus losses its long range mesoscopic order and thereby limits its further applicability. Even though, the wall thickness of the M41S materials can be improved by various post-synthesis modifications on the silica surfaces it seems to be a better alternative to take care on the synthesis

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* Corresponding author. Tel.: +91 20 25893761; fax: +91 20 25893761.
  E-mail address: apsingh@cata.ncl.res.in (A.P. Singh).

step itself, since it is known that the hydrolysis and condensation of various silica sources are altering and shows interesting properties with the gel pH and other pre-treatment conditions [6,10]. Hence, it is of tremendous importance to probe systematically the role of commonly used silica sources in the synthesis of metal-containing mesoporous materials at a particular pH and under a particular gel ratio, as it provides a qualitative idea about the active metal site isolations in various reported literature procedures and thus provide more insights in to the nature of interaction of the silica species with the structure directors, metal ions, etc.

In the present study, we describe the synthesis of two vanadium-containing mesoporous materials synthesized using fumed silica and tetraethyl orthosilicate silica sources and its detailed characterization to ascertain the mesostructural ordering and the nature of the vanadium sites. Furthermore, in order to observe how these properties get differentiated in reaction, the catalyst are applied in the liquid phase oxidation reaction of 1-napthol using aqueous H_2O_2 as an oxidant and the heterogenity of the material was followed by a series of leaching studies.

2. Experimental

2.1. Synthesis procedure

Vanadium-containing MCM-41 molecular sieves and pure siliceous MCM-41 were synthesized hydrothermally, using vanadium sulphate as the vanadium source ($VOSO_4 \cdot 3H_2O$, Aldrich) and cetyl trimethyl ammonium bromide (CTMABr, Loba Chemie) as the structure director. The silica sources used were fumed silica (99.8%, Aldrich) and tetraethyl orthosilicate (98%, Aldrich).

2.1.1. Synthesis of V-MCM-41
Vanadium-substituted MCM-41 materials are prepared hydrothermally [11] using a gel composition of,

$$SiO_2: 0.018VO_2: 0.17Na_2O : 0.5CTMABr : 100H_2O$$

where SiO_2 stands for fumed silica or tetraethyl orthosilicate. The synthesis was carried out by the slow addition of vanadyl sulphate (Si/V = 55) to an alkaline solution of the silica source. After stirring for a definite time, calculated amount of surfactant dissolved in deionized water was added and the gel mixture was stirred for 5 h at ambient condition, and finally autoclaved at an elevated temperature of 100 °C for 4 days. After hydrothermal treatment, the solid material obtained was filtered, washed with deionized water and then dried at 100 °C for 2 h to obtain as-synthesized V-MCM-41 samples. The surfactant occluded inside the pores of the vanadium-containing mesoporous material was removed by calcination at 540 °C for 5 h at a temperature ramp of 1 °C/min. For the removal of surfactant, mild extraction process was also performed by stirring 1 g of the as-synthesized catalyst with an

ethanolic solution (150 ml) containing 2 g of concentrated HCl (36 wt.%) at a temperature of 60 °C for 6 h. For comparison purpose, the corresponding MCM-41 silica polymorphs was also prepared under the same synthesis conditions (pH as well as temperature), but without vanadium source. The vanadium-containing catalyst prepared from fumed silica source is designated as VMS, while the materials obtained from tetraethyl orthosilicate is represented as VMT.

2.2. Characterization

Powder X-ray diffraction patterns of the samples were recorded on a Rigaku D MAX III VC Ni-filtered Cu Kα radiation, $\lambda = 1.5404$ Å between $1.5°$ and $10°$ (2θ). The specific surface area, total pore volume and average pore diameter were measured by N_2 adsorption–desorption method using NOVA 1200 (Quanta chrome) instrument. The samples were activated at 200 °C for 3 h under vacuum and then the adsorption–desorption was conducted by passing nitrogen into the sample, which was kept under liquid nitrogen. Diffuse reflectance UV–vis spectra were recorded in the range of 200–800 nm by a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment, using $BaSO_4$ as the reference. Temperature programmed reduction was carried out on Micromeritics Autochem 2910 catalyst characterization system, equipped with a TCD detector. Typically, 100 mg of calcined sample was treated with 5% H_2/Ar gas mixture (20 ml/min) and allowed to flow through the reactor, and the temperature was increased to 800 °C at a heating rate of 10 °C/min.

2.3. Oxidation of 1-napthol

Oxidation reactions were performed in a stirred round bottom flask fitted with a water-cooled condenser, using 30 wt.% aqueous H_2O_2 as oxidant. The reactant mixtures, 1-napthol (6.93 mmol, Aldrich), oxidant (13.86 mmol, Loba Chemie) and acetonitrile (6 ml, E-Merck) solvent were added to 0.1 g of catalyst and heated at a constant temperature of 70 °C under magnetic stirring. After reaction, the reaction mixture was cooled to room conditions and the catalyst was separated from the reaction mixture by centrifugation. The oxidized products were analyzed by a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (5 μm cross-linked methyl silicone gum, 0.2 mm × 50 m) and were further confirmed by GC–MS (Shimadzu 2000 A) and authentic samples.

3. Results and discussion

3.1. Powder X-ray diffraction

XRD patterns of vanadium-containing mesoporous materials synthesized by different silica sources show some important differences in the intensity of the characteristic
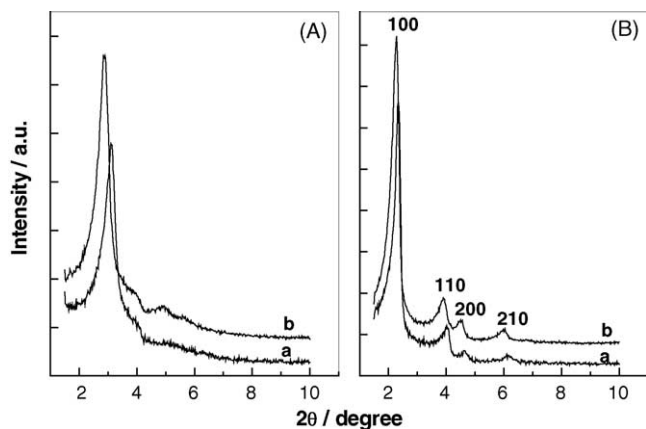
Fig. 1. X-ray diffraction patterns of (A) as-synthesized Si-MCM-41; (a) from fumed silica source, (b) from tetraethyl orthosilicate, (B) as-synthesized V-MCM-41; (a) VMS (55), (b) VMT (55).
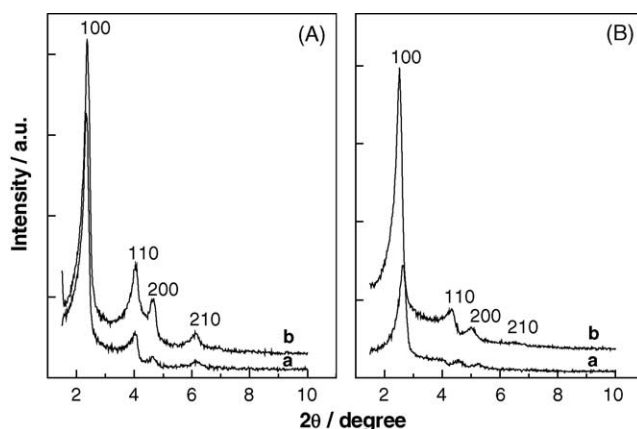

Fig. 2. X-ray diffraction patterns of (A) surfactant-extracted V-MCM-41 catalysts (a) VMS (55), (b) VMT (55), (B) calcined V-MCM-41; (a) VMS (55), (b) VMT (55).

diffraction patterns and long range ordering after various physical treatments. The well-defined XRD patterns of the as-synthesized V-MCM-41 samples prepared by using both silica sources can be indexed to the Bragg reflections, 1 0 0, 1 1 0, 2 0 0 and 2 1 0, characteristic of materials with hexagonal structure (Fig. 1B) and an increase in the unit cell values (a_o) compared with pure MCM-41 shows the incorporation of the vanadium in the molecular sieve framework, since the V−O bond distance is longer than the Si−O bond distance [5,11]. Thus, irrespective of the silica source, the as-synthesized V-MCM-41 materials had shown an almost similar XRD reflection pattern, with the presence of all long range ordered reflection peaks. Hence, in order to observe whether the increased ordering results from the nature of more condensed silica species or to the increased interaction between the silica species and surfactants, two common processes are opted for the removal of the occluded surfactants, viz. extraction and calcination. Interestingly, the samples obtained after extraction show an almost similar peak intensity and ordering (Fig. 2A), like the as-synthesized samples, while after calcination the material obtained from the fumed silica source shows a drastic decrease in the d_{100} peak intensity and in the intensity of characteristic long range ordered peaks (Fig. 2B). The increased intensity of the d_{100} peak after extraction, than the as-synthesized samples, may arise from the difference in density between the closed and

open structures of inorganic framework and surfactant, while maintaining the inorganic structural feature intact. However, the decreased intensity of the VMS catalyst after calcination, may arise due to the increased surface hydroxyl condensation which in turn may increase the wall thickness of the material and thereby its stability. Hence, the increased d_{100} peak intensity of the VMT catalyst even after calcination shows that a greater percentage of silanol groups are not vulnerable to condensation and these may have a reverse effect on its stability, during liquid phase oxidation reactions. These results are further supported from ^{29}Si MAS NMR and the results obtained are given in Table 1. Further, the absence of peaks above 20° (2θ) indicates that the as-synthesized/calcined samples are free from crystalline V_2O_5 [8].

3.2. N_2 physisorption analysis

N_2 adsorption–desorption isotherms of calcined vanadium-containing samples shows a sharp inflection at $P/P_0 = 0.2$–0.3 with completely reversible isotherms, and are of Type IV, characteristic of solids having uniformly sized mesopores. The specific surface area, pore volume and pore diameter of both V-MCM-41 materials and their silica analogous are listed in Table 1. From table, it is interesting to note that the surface area, pore diameter and the wall thickness of the V-MCM-41 materials are higher than their corresponding

Table 1
Physico-chemical properties of vanadium-containing MCM-41 materials

Sample	Si/V (final product)[a]	S_{BET} (m^2 g^{-1})	Pore volume, V_p (cm^3 g^{-1})	Pore diameter, D_p (nm)	Wall thickness[b], ω_t (nm)	$Q^4/(Q^3 + Q^2)$	TPR[c] T_{max} (°C)	AOS
SMS[d]	–	711	0.37	2.19	1.45	1.63	–	–
VMS	76	909	0.53	2.38	1.57	2.04	418	4.5
SMT[d]	–	905	0.56	1.93	1.60	0.84	–	–
VMT	102	1060	0.81	2.16	1.71	1.15	433	4.4

[a] Determined by ICP-OES analysis.
[b] Wall thickness $= a_o - D_p$, where $a_o = 2d_{100}/\sqrt{3}$.
[c] Temperature of maximum hydrogen consumption (T_{max}) and AOS is the average oxidation state values.
[d] SMS, Si-MCM-41 prepared from fumed silica source; SMT, Si-MCM-41 from TEOS as silica source.

silica polymorphs. Even though such results are unusual, they are meaningful in the sense that vanadium gets truly incorporated inside the silica framework positions and thus the increase in pore diameter may arise from the increased cationic size of V^{5+} ions (0.49 Å) than the Si^{4+} ions (0.26 Å) [12]. A comparison of these results with the XRD results further confirms this assumption as the vanadium-containing catalysts shows a better mesopore ordering than its pure silica counterparts, and hence, a summary of all the above characterization results shows that, in the present case, the uniform mesopore structural ordering gets increased in presence of metal salts.

3.3. Diffuse reflectance UV–vis spectroscopy

In order to extract the nature of vanadium species on the MCM-41 framework, DRUV–vis measurements were performed as it generally provides valuable information about the coordination environments and oxidation states of vanadium in various molecular sieves [7,8]. The as-synthesized V-MCM-41 materials are white in color while after calcination and exposed to ambient conditions, the materials gets yellowish and the color change is more prominent for the VMS catalyst than the VMT catalyst. Since the pore size of both materials are almost comparable, the abrupt color change of calcined VMS catalyst indicates a greater percentage of vanadium in the wall channels, where the water molecules can easily access the site for further coordination. Experimentally, the support material, MCM-41, shows a band at 220 nm typical of siliceous materials, but new bands are appeared at 260 nm and at 340 nm for V-MCM-41 materials and are attributed to the charge transfer (CT) bands associated with O^{2-} to V^{5+} in tetrahedral (T_d) environments. In detail, the band at 260 nm in the calcined VMS and VMT catalyst is attributed to the charge transfer transitions between tetrahedral oxygen ligands and the framework-substituted V^{5+} ions, while the band at 340 nm corresponds to vanadia species on the wall surfaces [13]. Further, the best peak fitting values show that ~85% of vanadium species are incorporated inside the framework of MCM-41 as tetrahedral species (peak at 260 nm) for VMT catalyst, while the VMS catalyst shows ~74% of tetrahedral species. These results shows the predominant formation of extra framework species when fumed silica is used for the synthesis of V-MCM-41 samples (Fig. 3). Moreover, absence of bands in the visible region (>400 nm) agrees well the absence of aggregated V_2O_5 species, as noted from the XRD results.

3.4. Temperature programmed reduction measurements

H_2-TPR reduction profiles of the catalysts taken in the 100–800 °C temperature range show that the reduction temperature maxima (T_{max}) and the average oxidation state (AOS) value varies for the VMS and VMT catalysts as given in Table 1 and visualised in Fig. 4. For comparison purpose, the reduction profile of pure V_2O_5 is also included (inset,
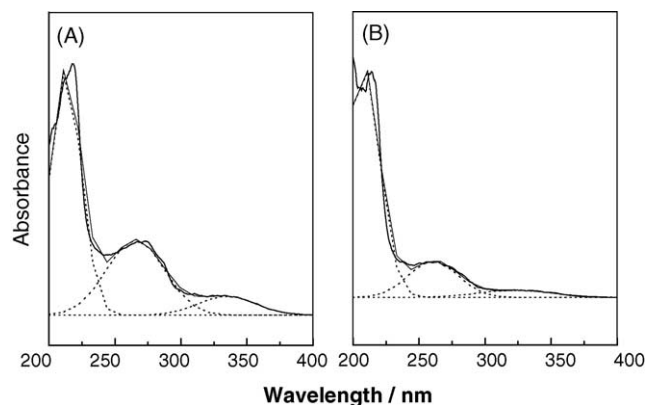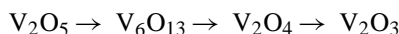

Fig. 3. DRUV–vis spectra of calcined V-MCM-41 materials: (A) VMS and (B) VMT.

Fig. 6). It was found that pure V_2O_5 exhibits multiple reduction profiles and the three peaks obtained are attributed to the reduction sequence:

$$V_2O_5 \rightarrow V_6O_{13} \rightarrow V_2O_4 \rightarrow V_2O_3$$

Various detailed studies performed over V/SiO_2 catalysts confirm that the reduction peak observed at 430 °C to surface dispersed tetrahedral vanadia phases and the peak observed after 500 °C for bulk-vanadia phases [14]. Usually, as the particle size of vanadia species gets increased, the vanadia species are more difficult to get reduce due to bulk diffusion limitations, resulting a shift in the reduction peaks to higher temperatures. In the present case, the maximum hydrogen consumption also falls in the 400–450 °C region, due to the reduction of monomeric or low oligomeric surface dispersed tetrahedral vanadia species, but a slight peak shift to higher temperature region is obtained for the VMT catalyst than the VMS catalyst [15,16]. Thus, from the present results, it can be concluded that both the catalysts contain tetrahedral
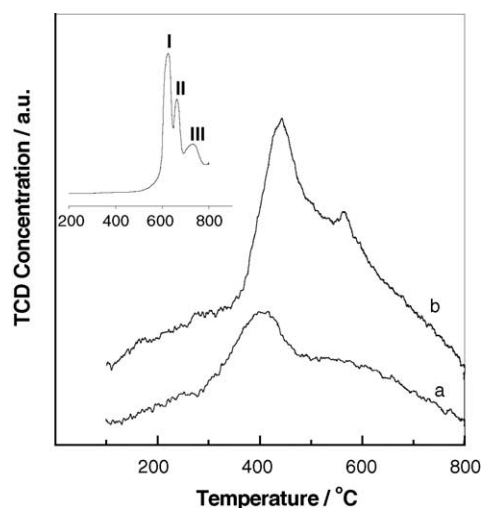

Fig. 4. H_2-TPR reduction profiles of (a) VMS (55) and (b) VMT (55); inset shows the spectra of pure V_2O_5.

vanadium species and were devoid from aggregated vanadia species [9].

4. Catalytic measurements

Various characterization techniques reveal that, regardless of the silica source, vanadium gets incorporated into the silica framework mainly as tetrahedral species and hence the catalysts may be active in the oxidation of aromatics using peroxides as the oxidizing source. Hence, the present catalysts, VMS and VMT, were screened in the oxidation of 1-napthol using aqueous H_2O_2 as an oxidant. The formation of 1,4-napthoquinone as the main product under both cases may stem out from the overoxidation of the primary product 1,4-dihydroxy naphthalene and hence the further formation of pthallic anhydride may arise reasonably from the cleavage of 1,4-napthoquinone, showing the sequential nature of the present reaction. The formation of more oxidized derivatives arise due to the well utilization of H_2O_2 by the active tetrahedral vanadium sites prevailing inside the pore channels of MCM-41. These results are further supported by the almost null activity of the parent silica supports. Thus the enhanced catalytic activity of the vanadium-containing catalysts arises unambiguously due to the presence of vanadium species present in the support, and the slight variation in activity between VMS and VMT catalysts may relates to the difference in the mesopore structural ordering and/or to the percental difference between the framework and extra framework metal species.

In order to verify whether the treatment conditions had an effect on the catalyst activity and stability, we had done reaction with the surfactant-extracted and calcined forms of VMS and VMT catalysts (Fig. 5A and B). Interestingly, no pthallic anhydride was detected for both the extracted catalysts but a greater percentage of hydroxylated products and 1,4-napthoquinone is observed (Fig. 6A and B). Hence, the deep oxidation activity of the catalysts after calcination may

Fig. 6. Product distribution with respect to catalyst treatment conditions: (A) VMS (55) and (B) VMT (55), where CAL denotes calcined, EX denotes surfactant-extracted catalysts, NQ denotes napthoquinone and PTA denotes pthallic anhydride.

arise from the greater percentage of surface dispersed extra framework metal species, which usually formed from the cleavage of the V−O−Si bonds during calcination procedures due to the presence of water formed during template decompositions [9]. These observations are more significant for the VMS catalyst and thus shows intense yellowish color for the hydrated calcined catalyst than the VMT catalyst. Hence, the increased conversion rates obtained for both catalysts after calcination show an average of active tetrahedral sites prevailing in the pore entrance of the catalysts, while for the surfactant-extracted catalysts as a large part of the active sites resides deep inside the silica framework they remain unapproachable for the diffused reactant species. Further, in order to observe whether the solvents had any influence on the catalytic activity and heterogenity of the vanadium-containing catalysts, the catalysts were screened broadly by using solvents like acetonitrile, acetone and ethanol. From Fig. 7, it is apparent that the conversion rates were more in aprotic solvents and the catalytic activity follows the order, $CH_3CN > (CH_3)_2CO > C_2H_5OH$. However, using VMS as
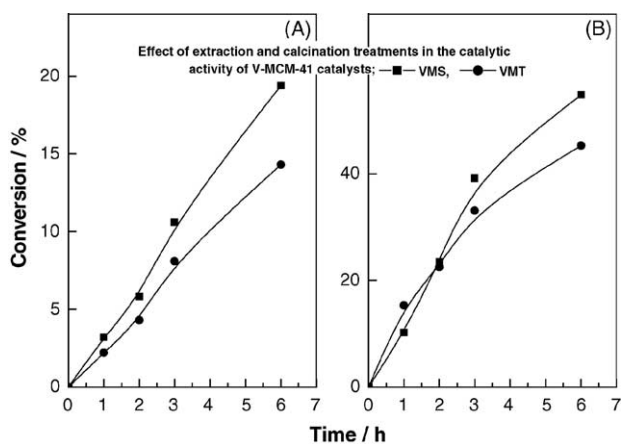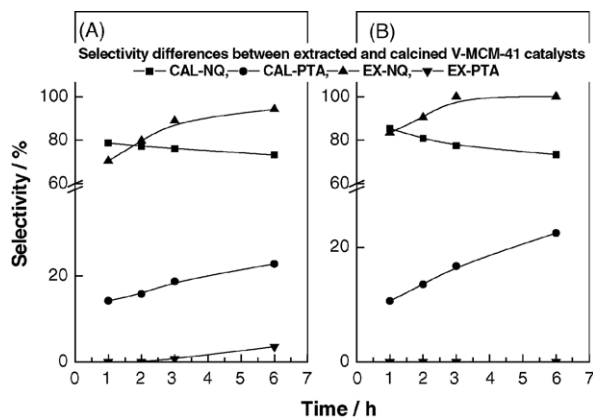

Fig. 5. Influence of treatment conditions towards the catalytic activity of V-MCM-41 catalysts: (A) after surfactant-extraction and (B) after calcination.
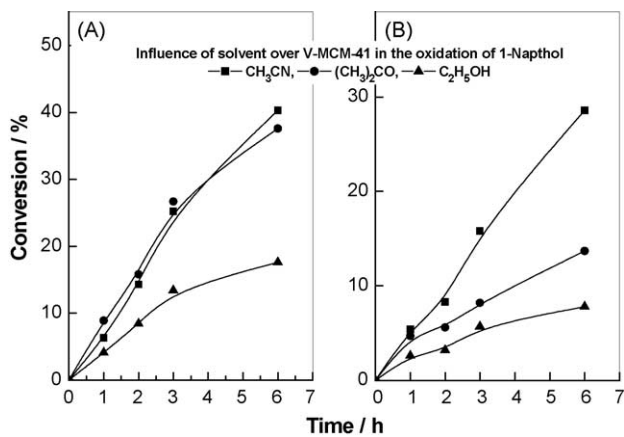

Fig. 7. Conversion profiles of V-MCM-41 catalysts in presence of different solvents: (A) VMS (55) and (B) VMT (55).

the catalyst, acetonitrile and acetone give almost similar conversion rates while changing the catalyst to VMT shows a dramatic difference between the two solvents. Thus, from the present results, a reasonable question develops that, whether the increased conversion rate observed for acetonitrile may relate to the strong interaction of solvent with the active vanadia sites, as the chelating ability of the solvents can drag some of the active extra framework metal species to the reaction mixture.

Hence, before concluding, it is necessary to check the stability of the catalyst under the present reaction conditions, since it can provide some relations between the wall thickness of the material, stability of extra framework species and the intactness of mesopore structure after the reactions. Literature reveals that vanadium and chromium-containing mesoporous materials show the leaching of active metal species during reactions and thus the enhanced catalytic activity may arise from the presence of such homogeneous leached metal species [17,18]. Hence, in order to attain a better insight into the catalyst behaviour, such a reaction condition was opted to check the heterogenity and further to verify the structural changes obtained for the mesoporous materials after the reaction. Since the leaching of active metal species during liquid phase oxidation reactions can arise from the coordination ability of the solvent, interaction of more aqueous oxidants on the defect sites and the stability of the mesoporous material, a series of leaching studies was performed to attain more evidence into the stability of the present catalyst systems [19]. Fig. 8 shows in detail the result obtained under various heterogenity studies (see footnotes for the procedures opted). Combining all these results, it can be ascertained that the solvent and oxidant had a deciding role in the leaching of the active metal species from both the vanadium catalysts, and

among them usage of aqueous H_2O_2 had a more detrimental effect on the stability of the present catalyst systems. Further, XRD patterns of the spent catalysts shows a decrease in intensity of the characteristic peaks with an almost disappearance of the long range ordered peaks and the changes are more prominent for the VMT catalyst than the VMS catalyst ($\sim$25% for VMS and $\sim$70% for VMT). Thus, even though the material prepared from TEOS silica source show more ordered structural pattern, after calcination, the hydrothermal stability of the material is worse under polar solvents. Thus the increased hydrothermal stability of fumed silica catalyst may arise from the increased silicate condensation during synthesis, and the more silanol condensation (increased wall thickness) occurred during the calcination treatments.

5. Conclusions

In conclusion, vanadium-substituted MCM-41 catalysts synthesized by using fumed silica and TEOS silica sources were characterized successfully by a series of spectroscopic techniques. Characterization data reveal the presence of more ordered structural patterns for the catalyst prepared with tetraethyl orthosilicate as the silica source, while catalytic activity results show that the catalyst prepared from fumed silica source is more active than the mesoporous vanadosilicate prepared from the tetraethyl orthosilicate source. It seems that the higher silicate condensation plus the presence of well-exposed active metal sites in pore channels are the two crucial parameters guiding the overall stability and activity of metallosilicates, which vary considerably with respect to the nature of inorganic backbone. Hence, the present study clearly demonstrates that various silica sources can change the overall structural and textural properties of metal-containing mesoporous materials, which in turn can affect the catalytic properties and stability of final mesoporous materials.
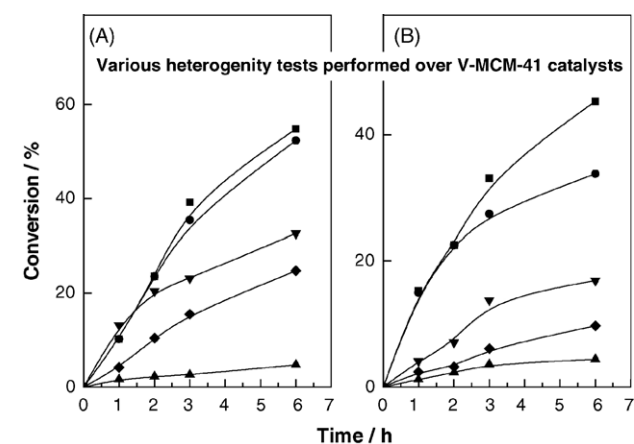
Fig. 8. Various leaching studies performed over V-MCM-41 catalysts: (A) VMS (55) and (B) VMT (55), where (■) fresh cycle, (●) submission of catalyst removed hot filtrate to the reaction conditions after 2 h of the run, (▼) submission of catalyst/CH_3CN/H_2O_2 stirred 'filtrate' to the reaction conditions with substrate, (♦) submission of catalyst/CH_3CN stirred 'filtrate' to the reaction conditions with 1-napthol and (▲) application of the solid 'catalyst' to the reaction condition, after stirring for 2 h in a $\sim$1 M H_2O_2 solution.

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