Vanadium incorporated mesoporous silicates as catalysts for oxidation of alcohols and aromatics

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Abstract

The present paper explores different synthesis conditions (direct hydrothermal synthesis or impregnation) for preparation of vanadium incorporated mesoporous silicate catalysts. Both hexagonal and cubic mesostructures have been obtained by varying the gel composition. All the prepared V-MCM-41 molecular sieves were tested in the oxidation of alcohols (hexanol, cyclohexanol and 1,3-hexanediol) and aromatic hydrocarbons (styrene and benzene) under mild conditions with hydrogen peroxide. The fresh (as-synthesized) and used samples after oxidation reactions were intensively characterized by X-ray diffraction (XRD), N_2 adsorption–desorption, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) techniques. The effect of the preparation conditions on the structure, texture, morphology and acidity of samples has been studied. The results show very low activity of all the V-MCM-41 catalysts in the oxidation of alcohols and high activity and selectivity in oxidation of styrene and benzene. It is interesting to note that the catalysts which are active in the oxidation of styrene to benzaldehyde will be less active in the oxidation of benzene to phenol and vice versa, suggesting that active centers for oxidation of styrene might probably be different to those for oxidation of benzene.
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1. Introduction

The molecular sieves with transition metals incorporated into the lattice have attracted increasing attention owing to their remarkable catalytic activity for partial oxidation of hydrocarbons under mild conditions [1,2]. MCM-41 molecular sieves, with high surface area, porosity and a large number of silanol groups

offer the possibility to graft the active species such as organometallic complexes on the internal surfaces of mesopores or to incorporate directly the metal ions inside the mesoporous framework by substitution of Si atoms in regular tetrahedral positions. A higher concentration of isolated vanadium active sites in the ordered mesoporous lattice can be obtained compared with the conventional silica support.

Vanadium modified molecular sieves have been largely studied and prepared by direct hydrothermal treatment [2–9], or by impregnation methods [10]. In these vanadium modified mesoporous molecular sieves were evidenced atomically dispersed vanadium centers and two oxidation states and coordinations

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[4,5,10,11]. The presence of two different types of vanadium species (two tetrahedral V^{5+} species and two square pyramidal VO^{2+}) suggests the real incorporation of vanadium into different framework, one inside the wall and other on the wall surface of the MCM-41 structure. Vanadyl (V=O) groups are energetically favored for vanadium in the oxidation states of +4 and +5 [12]. Only these vanadium ions located on the wall surface can reach a coordination number higher than four and can carry out reversible redox cycle. Reduction of V^V species in the framework position to neutral V^{IV} species can be realized by cleavage of a V–O–Si linkage. This new class of materials has a catalytic potential for selective oxidation of large organic molecules as cyclododecan, 1-naphtol [3], phenol and 2,6-di-*tert*-butylphenol [9], alkanes [13], benzene [14,15], naphtalenes, alcohols and tioethers [16].

In this paper we report the synthesis and characterization of vanadium modified hexagonal and cubic mesoporous silicate catalysts. Effects of the synthesis parameters on the structure and morphology will be discussed. The catalytic activity and selectivity of the vanadium modified mesoporous silicates have been tested in oxidation of alcohols and aromatic hydrocarbons with hydrogen peroxide. We try to establish on molecular level the relationship between the characteristics of catalysts and their catalytic properties.

2. Experimental

2.1. Synthesis

Vanadium modified mesoporous MCM-41 molecular sieves (VNS and VNT) and pure MCM-41 silica (N) were directly synthesized by hydrothermal synthesis in a temperature range of 373–433 K. The reagents used for synthesis were: tetraethylorthosilicate (TEOS) from Fluka, sodium silicate (25.5–28.5% silica) from Merck, tetramethylammonium hydroxide (TMAOH solution 25 wt.% in water) and cetyltrimethylammoniumbromide (CTMAB) from Aldrich, $VOSO_4 \cdot 5H_2O$ from Fluka and vanadium acetylacetonate from Aldrich. The solvents and other reagents for synthesis such as ethanol and 2-propanol from Merck, NaOH from Aldrich and H_2SO_4 from Merck were also utilized.

Two synthesis procedures by hydrothermal method, differing in the silica source, sodium silicate (VNS series) and TEOS (VNT series), were employed. For VNS series, 3.8 g of sodium silicate was added under stirring in aqueous suspension of 2.8 g CTMAB. After 4 h stirring at room temperature, a solution of TMAOH and NaOH (VNS1) or TMAOH (VNS2, VNS3 and VNS4) was added. The pH was adjusted to 10.5 with H_2SO_4 solution. For the VNS3 sample, alcoholic $VOSO_4$ solution and for other VNS samples, however, aqueous $VOSO_4$ solution were utilized. The resulted gels were loaded into Teflon-lined steel autoclave and heated at 373 K for 3 or 5 days.

In the second method (VNT series), $VOSO_4 \cdot 5H_2O$ powder was added to the TEOS/ethanol/2-prophanol solution. This slurry was mixed under stirring with another solution obtained from CTMAB, water and H_2SO_4. The pH was modified to 13 with NaOH solution (for VNT1 and VNT2 samples) and to 11 with NH_4OH (for VNT3 and VNT4 samples). In the case of VNT2 sample, the solution of the silica precursor and surfactant was introduced by drop wise in the NaOH solution. The gels were sealed into autoclave and heated at 433 K (VNT1 and VNT2) or 373 K (VNT3 and VNT4) for 3 days. The pH of the gels for the synthesis of VNT1 and VNT2 samples was further modified to 11 with H_2SO_4. These gels were subjected to another 3 days hydrothermal treatment at 373 K. Molar composition of all the gels loaded into autoclaves are presented in Table 1. The solid products were recovered by filtration and then washed with water and dried in air at 373 K for 12 h. The calcination was carried out 1 h at 773 K in flow of N_2, followed by 8 h in air to remove all the organics. The concentration of the metal into the vanadium modified mesoporous silicates was varied between 1.0 and 3.4 wt.%. For example, the V content in VNS1, VNS4, VNT1, NVT2 and VNT4 is around 1.6 wt.% and in VNS2, VNS3 and VNT3 around 3.4 wt.% and in VNI around 1.2 wt.%.

For comparison, V impregnated MCM-41 material labeled as VNI was also prepared. The catalyst with 1.2 wt.% vanadium was obtained by impregnation of the MCM-41 powder with a solution of vanadium acetylacetonate in tetrahydrofurane. The slurry was stirred and refluxed for 3 h at 343 K. The solid was filtered at room temperature, washed with

Table 1

Molar composition of the gels, textural and structural characteristics of the V-MCM-41 samples

Sample	Molar composition of the gels	$Na_2O/$ SiO_2	Surfactant/ SiO_2	S_{BET} $(m^2\,g^{-1})$	Φ (nm)	d_{100} (nm)	a_0 (nm)	w (nm)
VNS1	SiO_2:0.02V^{4+}:0.48CTMAB:0.9Na_2O:3.7TMAOH:nH$_2$SO$_4$:196H$_2$O	0.90	0.48	1055	2.7	3.6	4.16	1.5
VNS2	SiO_2:0.04V^{4+}:0.48CTMAB:0.48Na_2O:3.7TMAOH:nH$_2$SO$_4$:139H$_2$O	0.48	0.48	974	3.0	4.1	4.75	1.8
VNS3	SiO_2:0.04V^{4+}:0.48CTMAB:0.28Na_2O:3.7TMAOH:4.2Pr^{i}OH:nH$_2$SO$_4$:196H$_2$O	0.28	0.48	875	2.9	3.9	4.58	1.7
VNS4	SiO_2:0.02V^{4+}:0.48CTMAB:0.28Na_2O:3.7TMAOH:nH$_2$SO$_4$:139H$_2$O	0.28	0.48	965	2.9	4.0	4.63	1.7
VNT1	SiO_2:0.02V^{4+}:0.2CTMAB:0.92Na_2O:6.3EtOH:1.0Pr^{i}OH(0.05+n):H$_2$SO$_4$:196H$_2$O	0.92	0.20	1245	2.5	3.5	4.16	1.7
VNT2	SiO_2:0.02V^{4+}:0.2CTMAB:0.92Na_2O:6.3EtOH:1.0Pr^{i}OH(0.05+n):H$_2$SO$_4$:196H$_2$O	0.92	0.20	976	2.4	3.4[a]	_[b]	_[b]
VNT3	SiO_2:0.04V^{4+}:0.2CTMAB:9.1NH$_4$OH:6.3EtOH:1.0Pr^{i}OH:0.05H$_2$SO$_4$:nNa$_2$O:196H$_2$O	–	0.20	831	2.7	4.1	4.72	2.0
VNT4	SiO_2:0.02V^{4+}:0.2CTMAB:0.7Na_2O:6.3EtOH:1.0Pr^{i}OH(0.05+n):H$_2$SO$_4$:102.4H$_2$O	0.70	0.20	1032	2.8	3.9	4.55	1.7
VNI	SiO_2:0.48CTMAB:0.28Na_2O:3.7TMAOH:222.0H$_2$O	0.28	0.48	878	2.8	4.0	4.60	1.8
N	SiO_2:0.48CTMAB:0.28Na_2O:3.7TMAOH:222.0H$_2$O	0.28	0.48	1123	2.7	3.7	4.33	1.7

Moles added for the pH correction (n), wall thickness (w).

[a] First reflection line observed.

[b] No calculated due to the cubic structure.

tetrahydrofurane to remove salts in excess, dried and calcined at 773 K in a flow of N_2 and then air.

2.2. Characterization

The obtained materials were characterized by X-ray diffraction (XRD) (Philips PW 170 diffractometer), N_2 adsorption/desorption (Tristar, Micromeritics), scanning electron microscopy (SEM) with a Philips XL-20 microscope, transmission electron microscopy (TEM) with Philips Tecnai microscope, Fourier transform infrared spectroscopy (FTIR) (Spectrum 2000, Perkin-Elmer) and TG-DSC analysis (Setaram). The adsorption of ammonia was realized in an IR cell with self-supported sample wafers. A known amount of ammonia was introduced into the IR cell, after 1 h equilibration at room temperature. The spectra of adsorbed phases were then recorded by FTIR.

2.3. Catalytic experiments

The vanadium mesoporous molecular sieves were tested in oxidation of alcohols (hexanol, cyclohexanol and hexanediol) and aromatic hydrocarbons (styrene and benzene) with hydrogen peroxide. The catalytic oxidation reaction was performed using both a teflon autoclave (for oxidation of cyclohexanol on VNS catalysts) and a round bottom flask with magnetic stirring for 12–48 h in a temperature range of 296–343 K using an oil bath. An amount of 12 g of reactants, solvent and oxidant with a molar ratio of organic substrate/acetonitrile/H_2O_2 (30%) = 1/3.6/3 (styrene) or 1/-/3 (alcohols and benzene), and 70 mg of the catalyst were used. The oxidation of alcohols and benzene was made without solvent. After the separation of the catalyst by centrifugation, the analysis of the oxidation products was performed using a Carlo Erba gas chromatograph with a 3.5 m stainless steel column (i.d. 3 mm) containing OV-101 connected to a FID detector. The amount of the H_2O_2 was quantitatively analyzed by conventional iodometry. The used catalysts were dried at 373 K for 8 h and then used for recycling experiments. The active component leaching during the reaction was verified by resubmission of filtrates to reaction conditions. The used catalysts were also characterized by TEM, SEM and FTIR.

3. Results and discussion

3.1. Structural, textural and morphological characterization

X-ray diffractograms (Fig. 1) of all the samples synthesized with sodium silicate as silica source are characterized by three distinct reflection lines in the small angle range, representative of MCM-41 type mesoporous materials with the hexagonal arrangement of mesopores. The unit cell parameters are calculated and listed in Table 1. Higher intensity of reflections, (1 0 0), (1 1 0) and (2 0 0) are observed for VNS3 and VNS4 samples with lower Na_2O/SiO_2 molar ratio in the gels (Table 1). In general, the diffractograms of samples with shorter synthesis time (3 days) such as VNS1 and VNS2 show less intense reflections in comparison with the materials with synthesis time of 5 days such as VNS3 and VNS4, indicating that VNS3 and VNS4 samples have a more ordered structure than that of VNS1 and VNS2. The X-ray diffractograms of the samples synthesized with TEOS as silica source (VNT1, VNT3 and VNT4) are also characterized by reflections corresponding to the hexagonal arrangement of mesopores. The XRD pattern of the VNT2 sample (inset of Fig. 1), however, suggests the presence of a cubic phase. Effect of the Na_2O/SiO_2 molar ratio on the structure is less pronounced for the
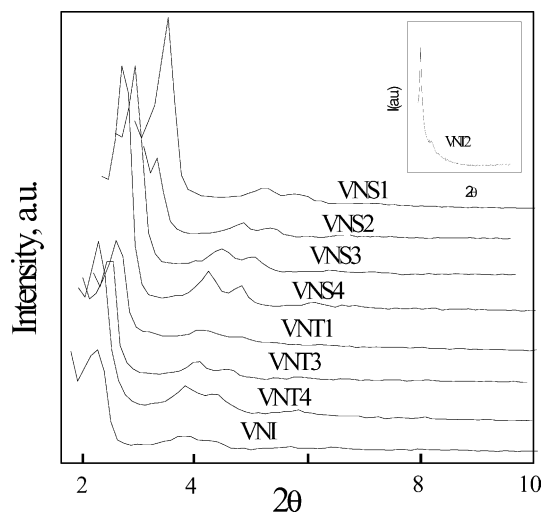

Fig. 1. X-ray diffractograms of a series of V-MCM-41 mesoporous molecular sieves.

samples synthesized with TEOS (Fig. 1). It is clear that the V-modified mesoporous samples synthesized with TEOS as silica source are less well ordered in structure compared to those synthesized with sodium silicate as silica source. This observation is quite contrary to our recent results that in the preparation of single metallic Nb or bimetallic Nb–Co modified mesoporous MCM-41 samples, the mesostructures obtained with TEOS as silica source is much more regular than those obtained using sodium silicate as silica source [17]. This suggests very clearly that in addition to the nature of silica precursor which plays a very important role in the organization of mesostructures, the final mesoporous structures are closely linked with type of metal ions. In fact, different synthesis conditions can affect the chemical state of metal ions in the gels. It is well known that the metal ions can more or less complex with amphiphilic surfactant molecules [18] (here CTMABr). This complexation can reinforce or disturb the well ordered micelles and thus conduct to more or less ordered mesoporous structures. The possibility or strength of complexation between the metal ions and surfactant molecules depend on the stability, type and form of metal ions in the gels which depend on the synthesis conditions. Although the molar composition of CTMAB is different in synthesis of VNS (0.48) and VNT (0.2) samples, we do not think that the different regularity obtained for VNS and VNT samples is due to this difference since we obtained highly ordered Nb-MCM-41 structure with TEOS and a molar composition of CTMABr equal to 0.2. The regularity of final silica mesostructures are thus related to the type of metal ions, nature of silica source and other parameters of synthesis such as molar ratio of surfactant/SiO_2, pH of the gel, temperature, etc.

The vanadium impregnated sample (VNI) gives also a XRD pattern with three distinct reflection lines in small angle range, however they are less well resolved compared with those by direct hydrothermal synthesis, indicating a relatively less well ordered MCM-41 type structure of VNI sample. VNI sample shows an increase in d_{100} spacing and in the unit cell parameter (a_0) compared with the corresponding pure MCM-41 silica (N) prepared by the same procedure. Because of the V–O bond distance longer than that of Si–O, some authors [7,8] have taken the increase in unit cell parameter as an indication of the incorporation of vanadium in the molecular sieve framework. However, we have

to take care when using this indication since sometimes, a unit cell contraction can be observed even though a notable amount of metal ions is incorporated in the framework. The synthesis conditions have to be taken also into account. We will discuss this in details in the following paragraph. The increase in d_{100} and a_0 observed in V-impregnated sample in our present case can suggest that impregnation method can conduct the incorporation of part of vanadium species into the framework. This confirms also our previous supposition that the impregnation can introduce not only the extra-framework species dispersed on the internal surface of mesopores, but also the lattice species [2,3].

The planar distance d_{100} is lower for the samples with high Na_2O/SiO_2 molar ratio (VNS1 and VNT1) synthesized by direct hydrothermal method. In fact, it was observed that a high quantity of the electrolyte can increase the electroneutrality at the surface of the micelle [7], diminish the electrostatic repulsion of the ammonium head group and decrease thus the cell diameter. Therefore, the increase in unit cell parameter could be a direct proof, but is not the only proof of incorporation of metal ions in the framework. For a same concentration of vanadium species in the gel, a high NaOH concentration favors the incorporation of vanadium into framework.

The nitrogen adsorption–desorption isotherms have the characteristic shape of MCM-41 materials and show an inflection in the P/P_0 range of 0.3–0.38, representative of the well-known capillary condensation within uniform mesopores (Fig. 2). All the samples have a very high surface area. The pore size distribution obtained by BJH method of all the samples shows a very narrow mono-modal peak centered in the range of 2.5–3.1 nm (Table 1). The increase of the vanadium content due to the extra-framework vanadium species and the use of NH_4OH leading to the less well organization of structure can decrease specific surface area of the mesoporous molecular sieves.

The pore wall thickness (w) of the hexagonal mesoporous materials can be estimated by subtracting the pore diameter value from the hexagonal unit cell dimension (a_0). It is observed that the pore wall thickness is variable but is higher for VNT samples prepared with NH_4OH and for VNS samples with a higher V^{n+}/SiO_2 and lower Na_2O/SiO_2 molar ratio. After synthesis and calcination, all the V-MCM-41 samples are in white color. Exposure to air immediately
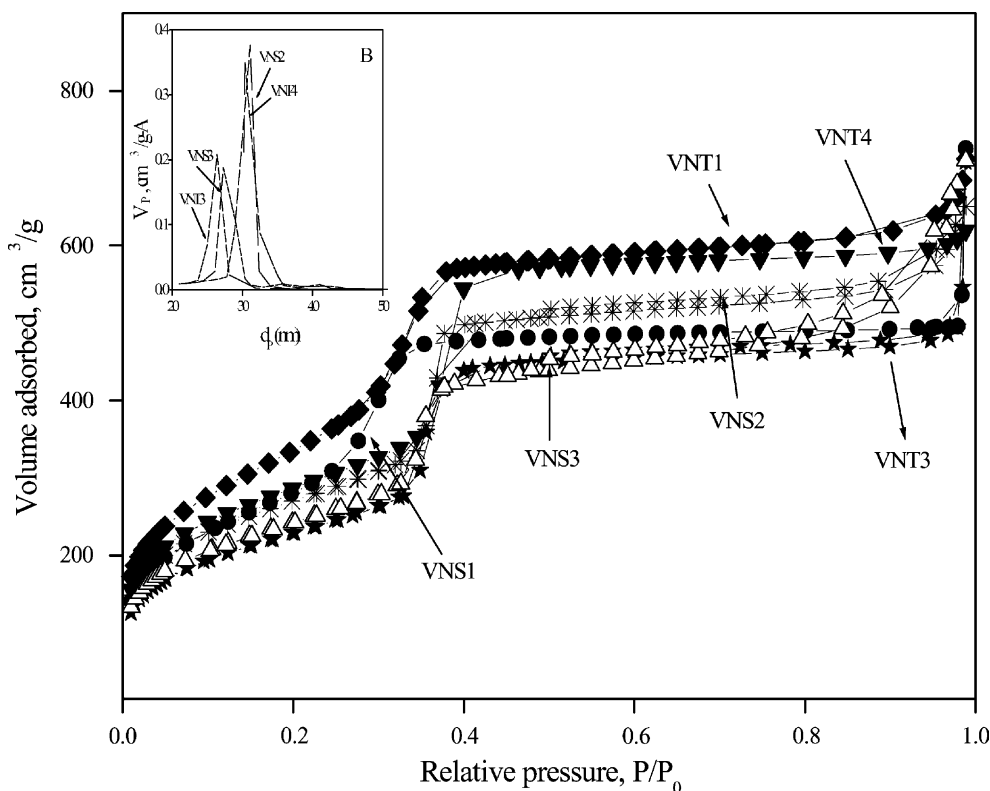
Fig. 2. N_2 sorption isotherms and pore size distributions of a series of V-MCM-41 mesoporous molecular sieves.

results in a yellow coloring, except VNS1 and VNS2 samples (synthesized with higher $NaOH/SiO_2$ molar ratio). This coloring is reversible. The change in color upon the exposure of calcined samples to air suggests the change in number of coordination of V species.

TEM images of V-MCM-41 materials, obtained both from TEOS and sodium silicate, show a very regular array of mesoporous channels in a hexagonal organization (Fig. 3). Comparing the XRD patterns (Fig. 1) and TEM images (Fig. 3) of V-MCM-41 samples obtained by direct synthesis and impregnation, it is obvious that pore structure becomes more disordered in the second case.

The morphology of these materials, illustrated by SEM (Figs. 4 and 5) is characteristic for the metals modified MCM-41 materials as previously reported [2,3] and consists of very small globular particles of $0.3–1.2 \, \mu m$ in diameter. The size of the globular particles resulted from the gel with a high Na_2O/SiO_2

molar ratio (Fig. 4a) is higher than those of the mesoporous V-MCM-41 materials obtained with a lower Na/SiO_2 molar ratio (Fig. 4b). Globular particles of the V-MCM-41 materials obtained by TEOS are even smaller and more homogeneous (Fig. 5) than the samples obtained from sodium silicate.

3.2. FTIR study

An amorphous structure of the wall, isolated silanols and hydrogen bonded OH groups are evidenced by IR spectroscopy after the calcination of vanadium modified samples in air atmosphere. The IR spectra (not shown here) of the calcined powders, obtained from TEOS (VNT1 and VNT4) or from sodium silicate with a lower Na_2O/SiO_2 (VNS3 and VNS4), show an increased intensity of the bands due to the symmetric Si–O stretching vibrations ($770–850 \, cm^{-1}$). These results indicate a higher concentration of siloxane groups and a high stability [19]
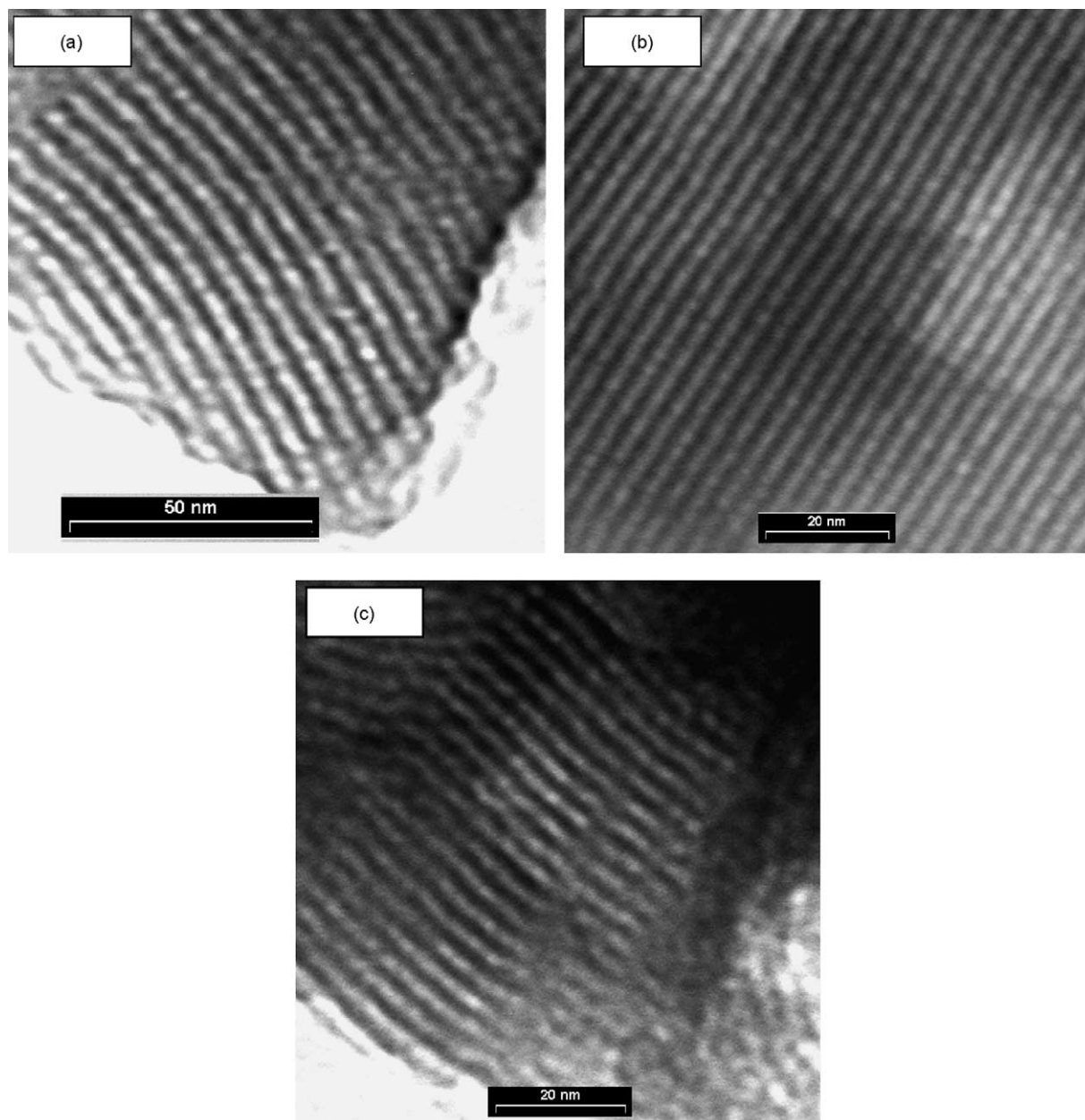
Fig. 3. TEM images of a series of calcined V-MCM-41 samples: (a) VNS1; (b) VNS2; and (c) VNI.

of all the VNT samples and VNS3 and VNS4 samples due to an increased network cross-linking. Intensity of the silanol vibrational bands at $3750\,cm^{-1}$ is higher for V-MCM-41 molecular sieves obtained by direct synthesis in comparison with the sample obtained by

impregnation of MCM-41. These results show, first, the incorporation of vanadium into the framework by direct synthesis and second, that V-MCM-41 molecular sieves obtained by direct synthesis have a high concentration of acid silanol groups (Fig. 6) same as
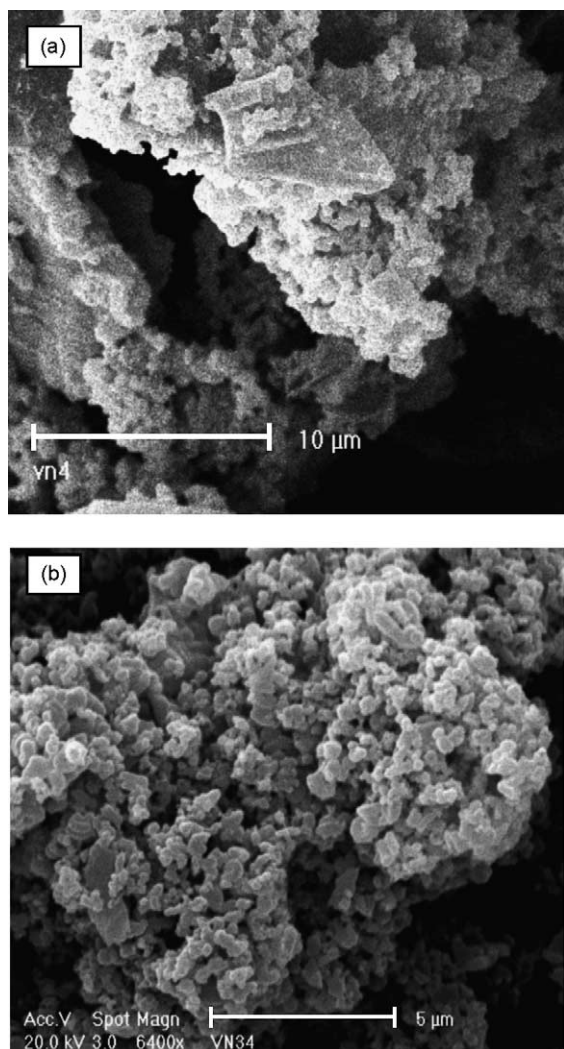
Fig. 4. SEM images of the calcined VNS samples: (a) VNS1; and (b) VNS4.

Fig. 5. SEM images of the calcined VNT1 sample.

observed in pure silicieous MCM-41 [2]. The incorporation of V species into the framework does not affect silanol groups. In contrary, the intensity of silanol groups is reduced when V species are introduced by impregnation. After adsorption of a defined ammonia onto the pretreated VNS1 sample, the intensity of silanol band decreases and a broad band centred at $3000 \, cm^{-1}$ and three bands at 3233, 3308 and $3398 \, cm^{-1}$ appear simultaneously. The broad band arises from the interaction between silanol groups of a V-MCM-41 sample and ammonia molecules.

This interaction reduces the O–H bond strength and shifts the OH bands toward lower wavenumber. This shift was previously observed in the adsorption of a series molecules such as benzene, ammonia and methylamine in zeolites [20–23]. The bands observed at 3233, 3308 and $3398 \, cm^{-1}$ correspond to the symmetric and anti-symmetric stretching vibration of N–H band. What we observe in the present work shows that the silanol groups after incorporation of vanandium species are still accessible and present a certain acidity.
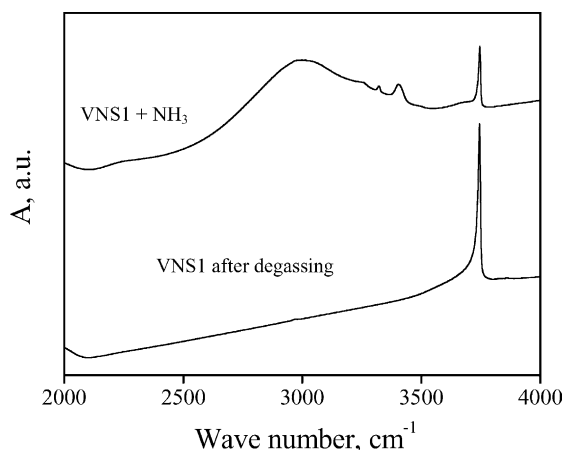
Fig. 6. IR spectra of the VNS1 sample after degassing (a); and after ammonia adsorption (b).

3.3. Catalytic activity in oxidation of alcohols and aromatics with H_2O_2

V-MCM-41 materials are active in oxidation of organic compounds [2]. The conversion and selectivity of V-modified mesoporous catalysts in the oxidation of hydrocarbons during 24 h reaction at 343 K are given in Table 2. Fig. 7 reports the variation in conversion of two catalysts synthesized with different silica precursors in oxidation of styrene (★) and benzene (■) as a function of reaction temperature. The general trend is that whatever the preparation method and whatever

Table 2
Catalytic activity and selectivity of V-MCM-41 mesoporous molecular sieves

Cat.	$C_{CH\text{-}ol}$ (%)	$C_{H\text{-}ol}$ (%)	Styrene			C_B (%)
			C (%)	S_{Bzald} (%)	$C_{eff.H_2O_2}$ (%)	
VNS1	1.2	0.4	5.6	84.5	3.3	10.2
VNS2	1.4	0.8	51.3	86.5	10.2	4.8
VNS3	4.2	2.1	78.6	54.2	12.2	60.4
VNS4	2.4	1.2	26.2	91.2	16.4	42.2
VNT1	1.2	0.7	18.4	74.5	18.2	8.2
VNT3	1.4	0.9	56.1	94.8	21.2	7.2
VNT4	7.2	3.8	13.4	76.2	10.3	57.3
VNI	0.7	–	20.2	84.5	7.8	14.2

Reaction conditions: Cat., 70 mg; molar ratio organic compound/solvent/H_2O_2 = 1/1.8/3 (styrene), 1/-/3 (cyclohexanol, hexanol and benzene); reaction temperature and time, 343 K and 24 h, respectively, in a glass flask reactor.
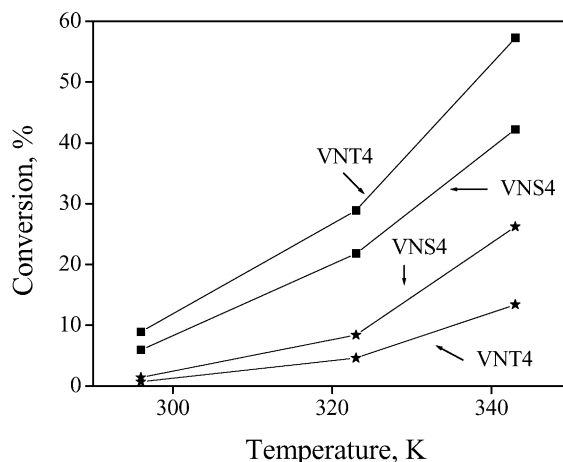

Fig. 7. Variation of the conversion with reaction temperature for VNS4 and VNT4 catalysts in oxidation of styrene (★) and benzene (■).

the V content is, the samples which are very active in hydroxylation of benzene will be however less active in oxidation of styrene (Table 2 and Fig. 7) and vice versa. The selectivity to benzaldehyde from styrene on all the samples is very high. The conversion of alcohols to aldehydes is also explored and shows to be very low and increases in the order: hexanol < cyclohexanol < 1,3-hexanediol. Comparing the catalytic results from two types of reactors, it is observed that in autoclave the conversion and efficiency of the H_2O_2 (H_2O_2 quantity used for oxidation/H_2O_2 quantity transformed) increase significantly. For instance, the conversion of cyclohexane is 14.5% and the efficiency of the H_2O_2 is 23.2% in autoclave at 343 K and 24 h of reaction while in glass flask reactors they are lower. This is very likely linked to the good imperviousness of autoclave reactor where a pressure slightly higher than atmosphere can be produced, favoring the conversion.

Comparing the catalytic behavior of three series of catalysts prepared by using sodium silicate and TEOS and by impregnation, the activity of VNI sample obtained by impregnation is lower. The V content in catalysts could be a key factor in conversion of styrene. It is found that for oxidation of styrene, the conversion increases with increasing V content for both series of catalysts (VNS and VNT). However, for hydroxylation of benzene, the preparation method can influence the activity of catalysts. For example, for the sample
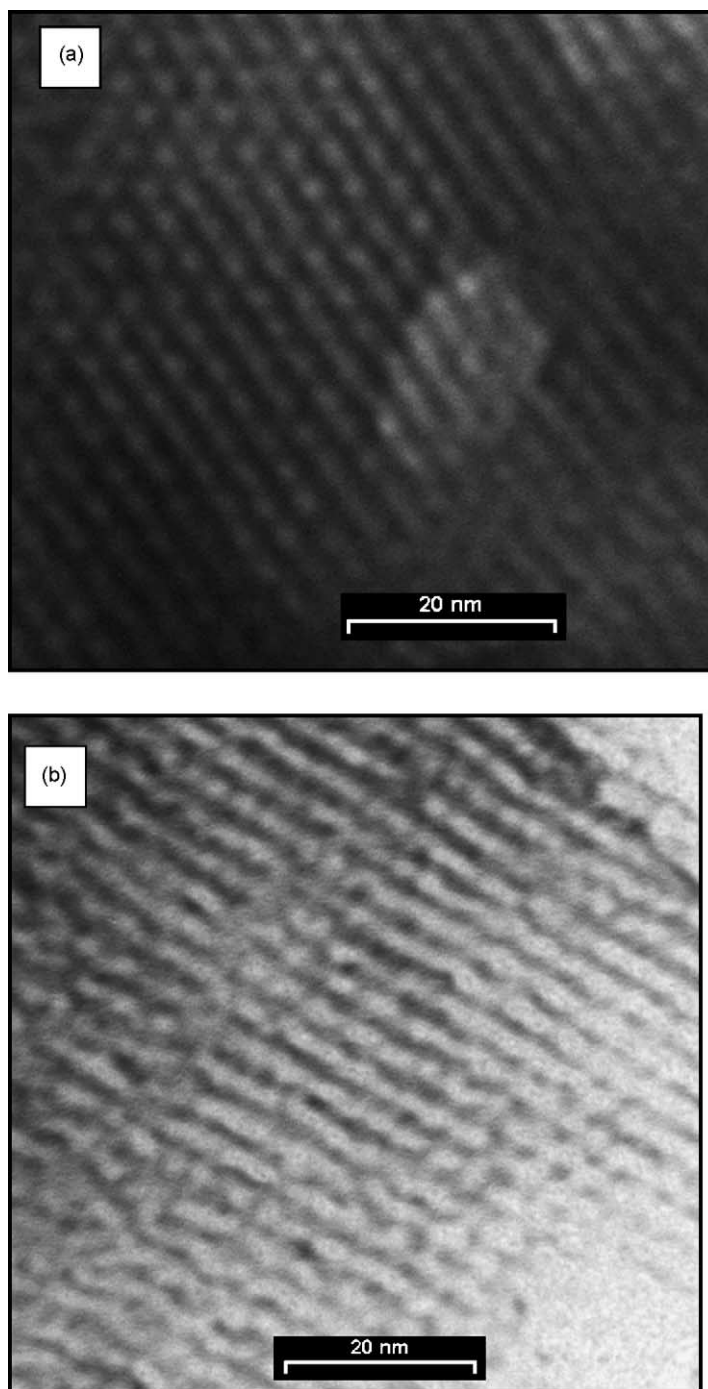
Fig. 8. TEM images of the VNS2 catalyst: (a) as-synthesized; and (b) after reaction.

having the same V content, VNT1 and VNT4, VNT4 sample has very high but VNT1 very low conversion of benzene. As discussed in Sections 2.1 and 3.1, VNT1 has been synthesized under 3 days hydro-treatment at 433 K (pH = 13) and then another 3 days at 373 K (pH = 11), while VNT3 has been hydro-treated only at 373 K 3 days (pH = 11). VNT3 has a better ordered mesostructure than VNT1 (Fig. 1). This could be the reason why VNT3 is more active in hydroxylation of benzene. Comparing the series of VNS, the same conclusion can be obtained. VNS3 and VNS4 have better organization of mesostructures (Fig. 1) than VNS1
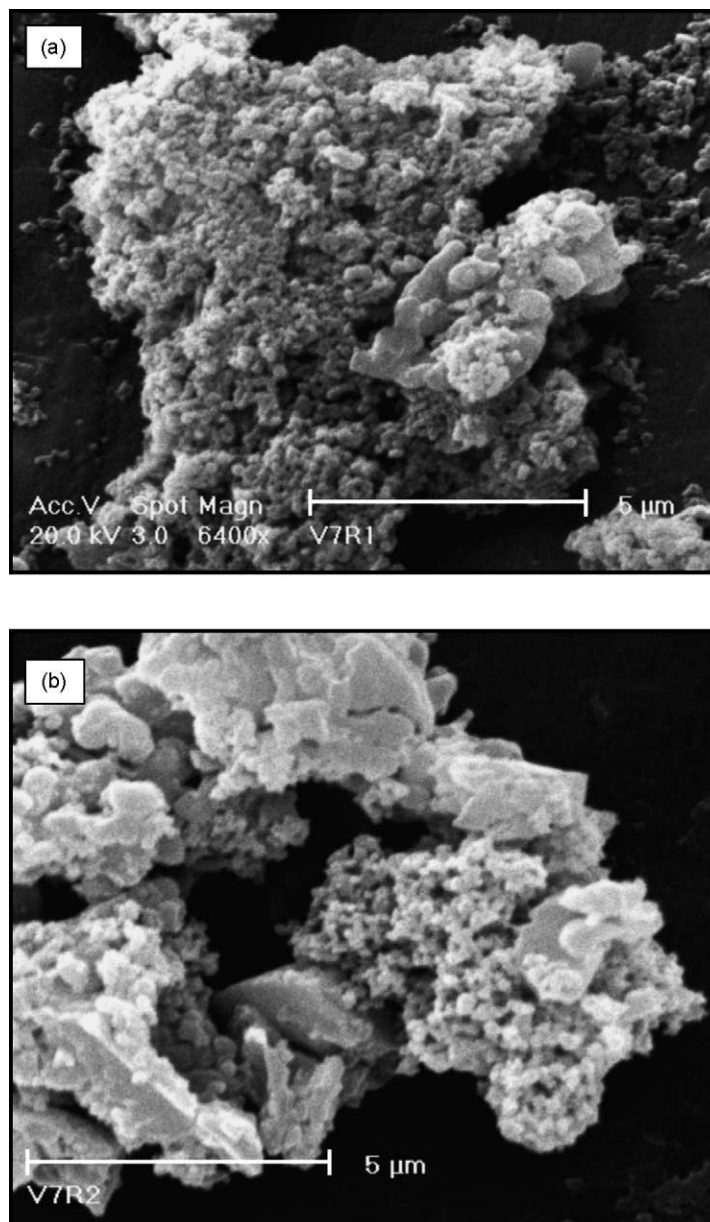

Fig. 9. SEM images of the VNT3 catalyst after reaction with benzene (a); and styrene (b).

and VNS2, therefore are more active. It seems that the ordering of mesostructure can affect the catalytic behavior of catalysts in hydroxylation and the V content plays only a secondary role.

It is obvious that high V content favors styrene conversion and high ordering of mesostructure leads to high hydroxylation of benzene. Since high V content conducts to a disordering of mesostructure, that is why the samples which are active for styrene oxidation will be less ordered due to high V content and will be less active for hydroxylation of benzene which needs an ordered mesostructure.

It has to emphasize that the benzaldehyde produced from the oxidation of styrene is due to the breaking of side chain, other than the benzaldehyde as main and desired product, methanol and its oxidation product formaldehyde are also formed. At the end of the reaction, some polycondensed products due to the polymerization of formaldehyde and/or benzaldehyde under present reaction conditions with the help of the V-modified catalysts are detected. However, in the oxidation of benzene, although the conversion is relatively low, the hydroxylation is the main reaction and phenol is the only product. That is why it is not necessary to list the selectivity values of this reaction in Table 2. In the oxidation of alcohols to their corresponding aldehydes or cetons, the same situation is noted.

3.4. Characterization of used catalysts

Used V-MCM-41 molecular sieves after reaction have been characterized by XRD, TEM, SEM and FTIR techniques. XRD and TEM (Fig. 8) analysis shows a less ordered structure after oxidation in liquid phase. This means that these samples have a less stability in conversion of hydrocarbons and the mesoporous structure of catalysts can be altered under the present reaction conditions. It was reported that a series of bivalent metal ions such as Fe, Co or Ni modified MCM-41 catalysts can conserve their ordered structure, indicating the high stability under reaction conditions of Fe, Co or Ni modified MCM-41 catalysts.

Variation of the morphology with solvent under the reaction conditions is evidenced by SEM (Fig. 9). In the absence of acetonitrile (biphasic system), the variation in morphology of particles is negligible, however, the efficiency of H_2O_2 decreases. This suggests that the presence of solvent can modify the internal structure, inducing a less ordered structure, and external morphology, changing the particle size and shape. However, the presence of solvent in several oxidation reactions is essential to have a high efficiency of H_2O_2. The reaction results using filtrates show that the leaching was insignificant for all the samples except VNT3 and VNS3 samples in which the V content is high. This suggests that for low V content samples, the V species incorporated in the framework are stable while in high V content samples, part of V species can be eliminated from framework.

4. Conclusions

Vanadium modified mesoporous silicates with a well ordered hexagonal and cubic structure were synthesized by direct synthesis or impregnation. The high specific surface, diameter of the pores, structure and morphology were comparable to the pure silica MCM-41. Vanadium ions were well incorporated inside of the silica wall and there is no direct interaction with silanol groups. V-MCM-41 mesoporous molecular sieves obtained by direct synthesis possess redox properties, but also a high amount of surface acidity evidenced by IR spectroscopy.

The catalytic properties of prepared V modified mesoporous catalysts in oxidation of hydrocarbons have been explored. The results showed that all the materials obtained are active and selective in oxidation with hydrogen peroxide of styrene to benzaldehyde and benzene to phenol. The activity in oxidation of alcohols is lower compared with that in oxidation of aromatic hydrocarbons. The conversion of alcohols increases when the reaction was performed in autoclave. It is obvious that catalysts containing V species are more suitable for oxidation of aromatics and other metal ions should be incorporated in mesoporous materials to have high activity in oxidation of alcohols.

A high ordered and stable hexagonal structure was obtained for the samples synthesized with sodium silicate and a lower Na_2O/SiO_2 molar ratio. These samples have a high catalytic activity.

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