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Mono (V, Nb) or bimetallic (V–Ti, Nb–Ti) ions modified MCM-41 catalysts: synthesis, characterization and catalysis in oxidation of hydrocarbons (aromatics and alcohols)

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Abstract

Mesoporous MCM-41 molecular sieves modified by single (V and Nb) or bimetal (Nb–Ti and V–Ti) ions with highly ordered hexagonal arrangement of their cylindrical channels were prepared by direct synthesis with two different silica sources (sodium silicate and TEOS) and characterized (as-synthesized samples and those used after reaction) by XRD, N_2 adsorption–desorption, TEM, SEM and FTIR techniques. Niobium and titanium were stabilized in the autoclavized gel by complexation with a ligand (acetylacetone and oxalic acid, respectively). V modified MCM-41 catalysts gave a very high activity in hydroxylation reaction of benzene and toluene and a low conversion in oxidation of styrene while Nb-modified MCM-41 samples showed very high conversion in oxidation of styrene but low oxidation conversion of benzene and toluene. Further introduction of titanium in V- and Nb-modified MCM-41 materials conducted to the less well-ordered hexagonal arrangement and gave very different effect on activity in oxidation of aromatics. Introduction of Ti into V-MCM-41 solids led to an increase in activity in oxidation of styrene and benzene but a decrease in conversion in oxidation of toluene. While the addition of Ti in Nb-MCM-41 resulted in a slight increase in conversion of styrene oxidation but a significant decrease in activity of benzene and toluene oxidation. It reveals that the introduction mode of oxidant in the reactors can also influence the activity and selectivity of reaction. An increase in reaction rate of oxidation, in the first 20 h, was obtained by introduction of H_2O_2 step by step during the reaction. The present paper evidenced that the side chain oxidation is main reaction of styrene oxidation while the hydroxylation is main reaction of benzene and toluene. That is why these two reactions need different catalytic centers as revealed by this paper. The oxidation of alcohols using V-modified MCM-41 as catalysts has also been explored and these catalysts showed a very low catalytic activity which increases in the order: hexanol $<$ cyclohexanol $<$ hexanediol.

Keywords: Mono (V, Nb) or bimetallic (V–Ti, Nb–Ti) ions modified MCM-41; Ammonia and benzene adsorption; Hydrogen peroxide; Styrene oxidation; Benzene and toluene hydroxylation

1. Introduction

The increasing needs of efficient and selective catalysts as well as the fundamental investigations are continuously the driving forces for synthesis of new molecular sieves. MCM-41 materials are mesoporous molecular sieves with a hexagonal array of uniform pores. Their silicate framework could be modified

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by partial isomorphous substitution with single or two transitional metals such as Ti, V, Cr, Fe, Co, Ni, Mn, Cu, La, Ru, Ni–Ru, Cr–Ni, V–Cu and V–Co [1–10]. Substitution with Ti is particularly interesting because of the success of Ti-substituted zeolites in the oxidation of various organic molecules [11]. Due to their larger pores compared to zeolite-based materials, metal ions incorporated mesoporous molecular sieves could be applied to the oxidation of bulky organic substances usually employed in the synthesis of fine chemicals [4–10,12–17]. The incorporation of two different metals might create materials with well-defined or new redox and acidic properties. Synthesis and catalytic application of such systems have been already reported [9,10,18,19]. It was known that acidic and catalytic properties of these materials depend on the localization and surroundings of the metal ions [9,10].

The present paper deals with the synthesis and characterization of high surface area V, Nb, VTi and NbTi-MCM-41 mesoporous molecular sieves by hydrothermal treatment. To better incorporate metal species such as Ti and Nb into the framework, a ligand-assisted templating method was employed. Ti(ac.ac)$_2$ and niobium complexed with oxalic acid or acetylacetone, respectively, were used as titanium or niobium precursors. The catalytic activity of all the samples prepared was evaluated in oxidation of styrene, benzene and toluene with hydrogen peroxide. The mode of H_2O_2 addition into the reactors was also studied. The oxidation of alcohols (hexanol, cyclohexanol and hexanediol) using V-modified MCM-41 samples was explored.

2. Experimental

2.1. Synthesis

The reagents used for the synthesis were sodium silicate (25.5–28.5% silica, Merck) cethyltrimethylammonium bromide (CTMABr, Aldrich), tetramethylammonium hydroxide (TMAOH solution 25 wt.% in water, Aldrich), $VO(SO_4)_2\cdot 5H_2O$ from Fluka, $NbCl_5$, Ti(ac.ac)$_2$ (Aldrich), 2-propanol (Aldrich), oxalic acid (Aldrich), NaOH and H_2SO_4 (Aldrich).

V-MCM-41 and Nb-MCM-41 materials were synthesized by two procedures, differing in the silica source. Method I (VNS, NbNS, VTiNS and NbTiNS samples) used sodium silicate as the silica precursor. V, Nb, VTi and NbTi-MCM-41 mesoporous molecular sieves were synthesized by this method using gels with the following molar composition: $1.0SiO_2$:xM^{n+}:0.48CTMABr:$0.28Na_2O$:3.7TMAOH:$222H_2O$ (where $x = 0.02$ for V, Nb and 0.04 for VTi and NbTi-MCM-41). The molar ratio of V/Ti and Nb/Ti was 1. A defined amount of alcoholic (2-propanol) $NbCl_5$ solution was introduced by dropwise in aqueous solution of oxalic acid. This solution with niobium or an alcoholic solution of $VO(SO_4)_2\cdot 5H_2O$ or Ti(ac.ac) was added to a mixture of 3.8 g sodium silicate, 2.8 g CTMABr and 30 g H_2O under stirring. After 2 h stirring, TMAOH solution was added. The gels obtained was sealed into Teflon-lined steel autoclaves and heated 5 days at 373 K. The pH value was adjusted to 11 with H_2SO_4.

Using Method II, V-MCM-41 and Nb-MCM-41 samples labeled as VNT and NbNT were synthesized with tetraethylortosilicate (TEOS), $VOSO_4\cdot 5H_2O$ or $NbCl_5$, ethanol, 2-propanol, oxalic acid and an acidified mixture of CTMAB in water. The molar composition of the gels was: $1.0SiO_2$:$0.02M^{n+}$:0.2CTMABr:$0.07H_2SO_4$:6.5EtOH:1.0 2-PrOH:$96H_2O$. The gels were loaded into Teflon link steel autoclave and heated at 373 K for 3 days. After this treatment the pH was adjusted to 11 and hydrothermal treatment was continued another 3 days at the same temperature. All the products obtained were filtered, washed and dried at 373 K and calcined in a flow of N_2 and then air at 773 K. From elemental analysis, for the single metal incorporation, metal content varies from 0.8 to 1.7 (Nb content is lower) and for bimetal ions incorporation, the total metal content varies from 2.4 (NbTi) to 3.4 (VTi).

2.2. Characterization

The structure of the samples was identified by using the Philips PW 170 diffractometer (Cu Kα radiation with power 40 kV, 30 mA) and a Tecnai-Philips transmission microscope (accelerating voltage was 100 kV). N_2 adsorption–desorption isotherms were obtained from the volumetric adsorption analyzer (Tristar or ASAP 2010, Micromeritics) and the pore diameter and the pore size distribution were determined by the BJH method from the adsorption branch of isotherm. The morphology of obtained phases was studied by using a Philips XL-20 scanning electron microscope (SEM). Infrared spectra were recorded with a Perkin Elmer Spectrum 2000 spectrometer in KBr pellets and in IR cell. The self-supported wafers of calcined samples (for benzene and ammonia adsorption) were loaded in an IR cell and pretreated under vacuum [20–23]. The known amounts of single compound (ammonia or benzene) were introduced at room temperature until saturation of the sample wafer. The spectra were recorded after each addition of adsorbate.

2.3. Catalytic experiments

The catalytic oxidation reaction was carried out in the presence or absence of the solvent (acetonitrile). The reaction temperature and time varied from 293 to 343 K and from 1 to 48 h, respectively. The molar ratio of aromatics/solvent/hydrogen peroxide was 1/–/3 for benzene and toluene and 1/–/3, 1/1.8/3 and 1/1.8/6, for styrene and 70 mg of the catalyst were used. The conversion and reaction rate as a function of reaction time in oxidation of styrene with VTi- and NbT-MCM-41 catalysts were measured. 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 an FID detector. The amount of the H_2O_2 was quantitatively analyzed by conventional iodometry and H_2O_2 efficiency (amount of H_2O_2 used in styrene oxidation/amount of H_2O_2 transformed) was calculated. Catalyst active component leaching during the reaction was verified.

3. Results and discussion

3.1. Structural, textural and morphological study

The structural properties of the V-, Nb-, VTi- and NbTi-MCM-41 mesoporous molecular sieves are, in general, identical to MCM-41 materials. As, all XRD patterns (Fig. 1) of the V- and Nb-MCM-41 (VNS, VNT, NbNS and NbNT) materials showed one major, assigned to reflection line of (1 0 0), and three small peaks, corresponding to reflection lines of (1 1 0), (2 0 0) and (2 1 0), respectively, in the small angle range, typically for an ordered hexagonal structure. Only the further introduction of titanium conducts to the less well-ordered hexagonal arrangement. The very ordered structure was obtained for the V and Nb samples synthesized by Method II (VNT and NbNT). This is quite in accordance with our very recent results that TEOS as silica source can favor the formation of better organized Nb modified mesoporous materials and that the incorporation of Nb into the framework could be favored with sodium silicate as silica source, but provoking a disorganization of structure [8–10]. The higher unit cell parameter a_0 (calculated from $a_0 = 2d_{1\,0\,0}(3)^{-1/2}$) obtained for the majority of the samples compared with pure MCM-41 silica is an indication [4] of the presence of metal ions in the molecular sieve framework (Table 1). Although the incorporation of metal ions can be favored when sodium silicate was used as silica source in the synthesis, the lower stability of $NbCl_5$ solution in the gel with sodium silicate (Method I) compared with alcoholic TEOS solution (Method II) explains a lower incorporation of the niobium ions into the network for the NbNS and NbTiS samples and their small unit cell parameter. The detection of Nb ions by chemical analysis method in the filtrate of the synthesis gel after hydrothermal treatment confirmed that in NbNS and NbTiNS samples, not all niobium ions present in the gel is build into the framework of MCM-41 structure during the hydrothermal treatment.

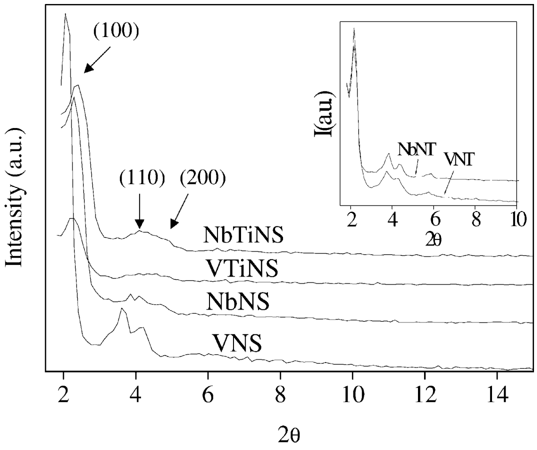

Fig. 1. X-ray diffraction patterns of V–Nb, VTi- and NbTi-MCM-41 mesoporous molecular sieves prepared from different methods.

Table 1
Characteristics of the mesoporous molecular sieves and their catalytic activity and selectivity in oxidation of aromatics[a]

Sample	a_0 (nm)	S_{BET} (m^2/g)	$Ø_{BJH}$ (nm)	W (nm)	Styrene			$C_{benzene}$ (%)	$C_{toluene}$ (%)
					C (%)	S_{Bzald} (%)	$Eff_{H_2O_2}$ (%)		
VNS	4.63	965	2.9	1.73	46.2	94.2	14.2	62.2	68.2
VNT	4.55	1032	2.8	1.75	23.2	86.2	10.3	67.3	67.1
NbNS	3.85	842	2.5	1.30	87.2	18.4	17.8	10.9	3.1
NbNT	4.63	912	2.8	1.83	86.6	98.5	30.4	1.2	1.8
VTiNS	4.35	1096	2.5	1.85	99.1	76.4	28.6	78.2	16.2
NbTiNS	4.27	827	2.9	1.40	89.4	95.8	34.2	1.4	0.9
NS	4.33	1123	2.9	1.63	na	na	na	na	na

[a] S: samples synthesized with sodium silicate and T: samples synthesized with TEOS, W: wall thickness = $(a_0 - f)$. Reaction conditions—reaction temperature: 343 K, reaction time: 48 h, catalyst amount: 70 mg, reactant/solvent/H_2O_2: 1/1.86/6 for styrene and 1/–/3 for benzene and toluene. C (%): conversion of reagent in oxidation reaction. S (%): selectivity of one product in oxidation reaction. $Eff_{H_2O_2}$ (%): efficiency of H_2O_2. Na: no activity.

Table 1 presents the variation of the specific surface area with unit cell parameters and pore sizes of obtained samples. All the VNS, VNT and NbNT samples have a very high surface area. The TEM pictures confirm the well-organized hexagonal pore system for these samples and a slight degradation of the structure for NbNS, NbTiNS and VTiNS samples (Fig. 2). TEM images of all samples show that the uniformly sized channels separated by silica walls are regularly packed in a hexagonal manner, with pore-to-pore distance of 4.6–4.2 nm, in good agreement with the XRD results. The BJH pore size distribution indicates a narrow and monomodal peak centered at around 2.8 ± 0.3 nm for all the samples (Table 1).

SEM pictures of all the samples are typical for the mesoporous metallosilicates and show a spherical morphology (Fig. 3). A variation of the morphology with composition of the materials and the synthesis method can be clearly visualized. The dimensions of the spheres are lower for all the samples synthesized with TEOS and higher for all the Nb or Nb–Ti samples.

The IR spectra were recorded in the 400–4000 cm^{-1} range for the calcined mono- and bimetallic incorporated mesoporous molecular sieves. The spectra of these materials demonstrate the framework vibration similar to those of amorphous materials, suggesting similarities in their local atomic arrangements (Fig. 4). The broad bands at around 3500 cm^{-1} may be attributed to water adsorption in our samples. The absorption bands at 1620–1640 cm^{-1} arising from bending vibrations of adsorbed water molecules confirm the presence of water molecules physisorbed in our samples. All the samples exhibit a symmetric stretching vibration band at around 801 cm^{-1} and the anti-symmetric vibration band at around 1080 cm^{-1} of the tetrahedral SiO_4^{4-} structural units. The presence of an infrared band at around 960 cm^{-1} appears to be the possible evidence of the isomorphous substitution of Si by metal ions. The interpretation of this band [24] is the stretching mode of SiO_4 units bonded to a transition metal cation or Si–O stretching vibration of Si–O···H. Furthermore, it is noticed that the anti-symmetric stretching band at ∼1080 cm^{-1} becomes less structured when niobium and titanium ions are introduced. This is taken as an indication of a loss in the structural regularity and in agreement with the XRD and TEM observation.

From characterization results by different techniques, although we have no direct prove, a series of indirect proves give us the solid indication concerning the incorporation of metal ions in the framework.

3.2. Benzene and ammonia adsorption properties

Adsorption of ammonia and benzene at room temperature has been carried out to investigate Brønsted and Lewis acidity potentially produced by the incorporation of heteroatoms in the silica matrix. The introduction of the metal ions in the MCM-41 silicas induces a modification in adsorption capacity of ammonia and benzene (Fig. 5). Adsorption of NH_3 (spectra not reported) shows that no strong Brønsted sites are present in vanadium-containing sample, as

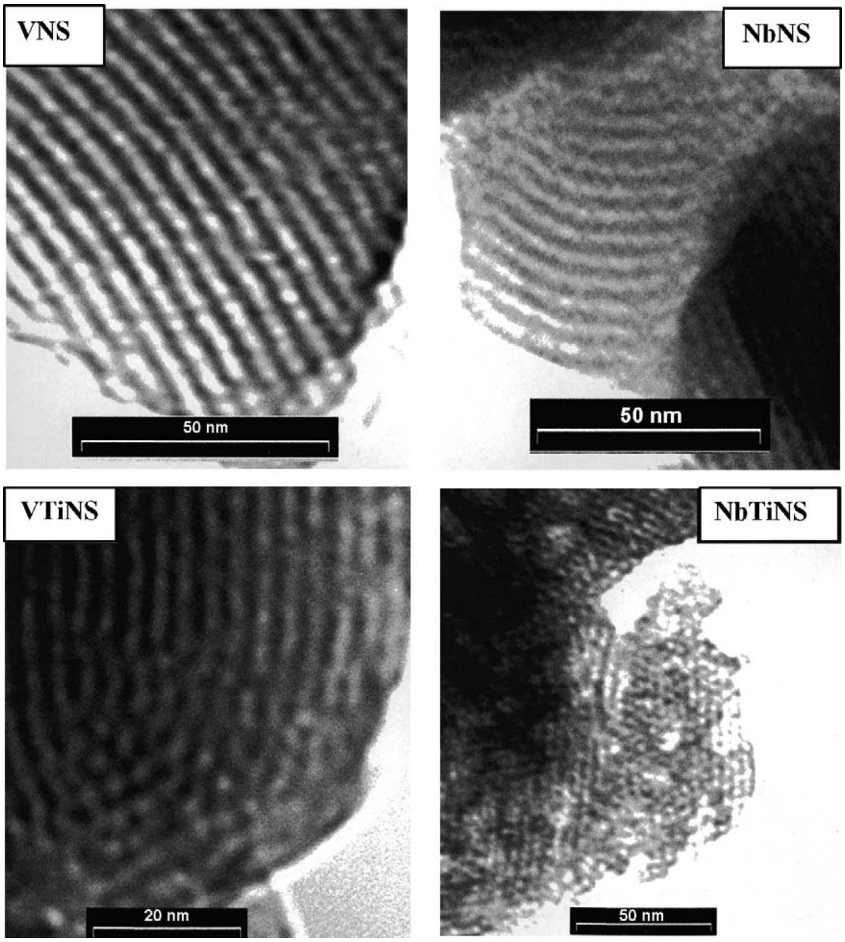

Fig. 2. TEM images of the calcined mono- (V, Nb) or bimetallic (VTi, NbTi) ions modified MCM-41 samples.

no ammonium ion is formed. A small amount of Brønsted sites, able to give proton transfer to ammonia are seen in the samples with niobium. Molecular ammonia adsorption is visible in the spectra of all the samples, due both to molecules coordinated to acidic Lewis sites and interacting via H-bonding with silanols. In order to study Lewis sites, benzene adsorption has been performed (Fig. 5). The negative feature at 3740 cm^{-1} is due to the interaction of silanols with benzene which shifts the silanol bands at 3740 cm^{-1} toward lower wavenumber, giving a broad band centered at around 3650 cm^{-1}. It is well known that the shift content can be used to evaluate the strength of acid sites [20–23]. With the help of Winspec program, we have measured the shift value of silanols due to the benzene adsorption. It can be seen that the shift value for all the studied samples after adsorption of benzene is quite similar, indicating the similar acid strength of all these metal ions modified samples and that the introduction of these metal ions does not affect, as least not significantly, the acidity of silanols. The presence of a series of peaks in the range 3000–3100 cm^{-1} (combination bands of C–C and C–H), two small peaks at 1960 and 1815 cm^{-1} (C–H out-of plan bending vibration) and sharp peak at 1480 cm^{-1} (C–C stretching mode) which result from the benzene molecules, indicates clearly the real adsorption of benzene on these samples. FTIR spectra recorded after adsorption of a similar quantity of benzene on VNS, NbNS, VTiNS and NbTiNS samples

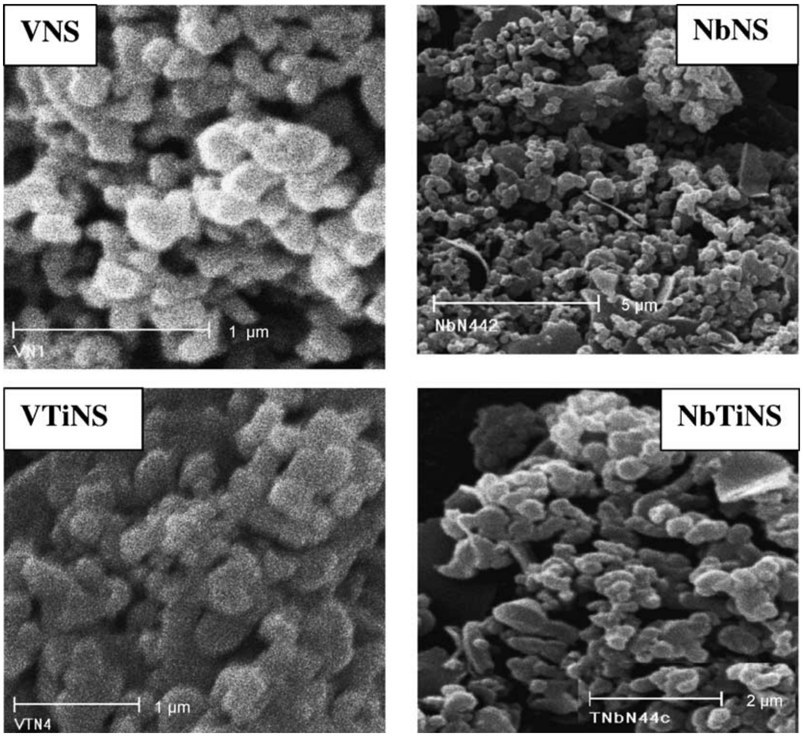

Fig. 3. SEM images of the calcined mono- (V, Nb) or bimetallic (VTi, NbTi) ions modified MCM-41 samples.

show a variable band intensity, thus variable adsorption capacity since the absorption intensity is directly proportional to the amount of benzene adsorbed on the basis of Beer–Lambert law [20–23]. Thus, the benzene adsorption capacity increases in the order: VNS < NbNS < VTiNS < NbTiNS. This suggests that the incorporation of (two) metal ions in the framework of MCM-41 molecular sieves can increase their benzene

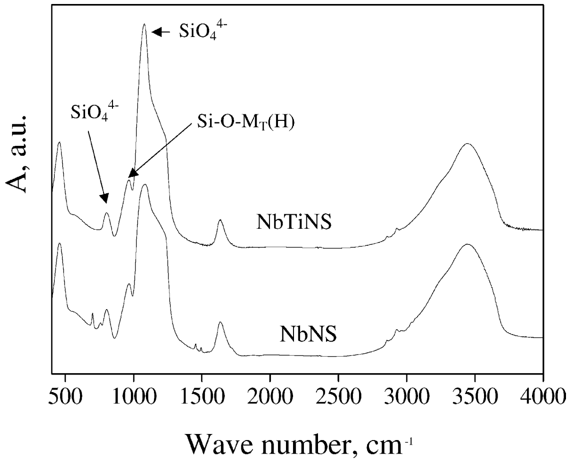

Fig. 4. FTIR spectra of the calcined samples (sample powders are dispersed in KBr pellets).

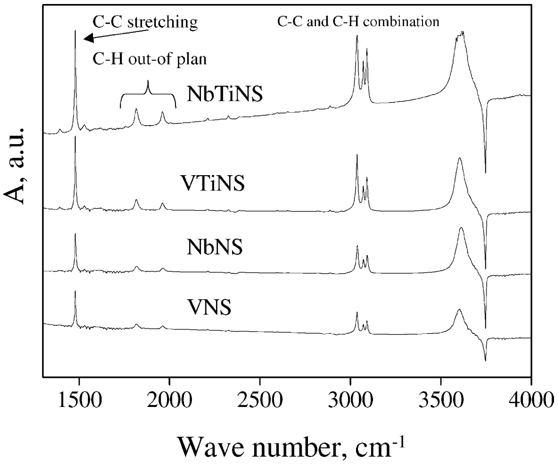

Fig. 5. FTIR spectra of the samples after benzene adsorption.

adsorption capacity and that these metal ions in the framework are the adsorption centers and accessible to aromatic molecules [11]. This could be another indirect prove of the incorporation of metal ions in the framework since only the metal ions in the framework but not metal oxides can have this kind of interaction with benzene molecule. The above discussion could be also very important in explaining the catalytic activity of these samples in oxidation of aromatics.

3.3. *Catalytic activity in oxidation of hydrocarbons (aromatics and alcohols)*

The catalytic activities of the V-, Nb-, VTi- and NbTi-MCM-41 mesoporous molecular sieves in oxidation of styrene, benzene and toluene with hydrogen peroxide are presented in Table 1. The oxidation reactions were realized during 48 h, at 343 K with 70 mg of the catalyst and 1/1.8/6 molar ratio (org.comp./solvent/H_2O_2) for styrene oxidation and 1/–/3 molar ratio for benzene and toluene oxidation. The catalysts modified with vanadium, whatever is the synthesis method (I or II), are very active in hydroxylation of benzene and toluene while these catalysts show very low conversion in oxidation of styrene. The catalysts modified with niobium have very high activity in oxidation of styrene while their conversion in oxidation of benzene and toluene is quite low. It has to indicate that the selectivity to benzaldehyde from styrene is higher for the catalysts synthesized with TEOS in the last case. Modification of the V-MCM-41 catalysts by incorporation of titanium increases significantly the activity in oxidation of styrene and benzene, but reduces the conversion of toluene. The VTiNS catalyst has the highest conversion in the oxidation of styrene and benzene. However, the introduction of Ti into Nb-MCM-41 materials does not significantly affect the conversion of styrene, the selectivity to benzaldehyde is sharply improved from 18.4 to 95.8%. The efficiency of the H_2O_2 is lower for the niobium-containing catalysts.

The above observation supplies important information that the active centers for oxidation of styrene might probably different to those for oxidation of benzene and toluene. In the conversion of styrene with H_2O_2, the oxidation of side chain, conducting the breaking of the side chain, is predominated while in the conversion of benzene and toluene, the hydroxylation is main reaction. The addition of Ti into Nb-MCM-41 can improve the selectivity in benzaldehyde. In the design of the efficient catalysts, we have to take into account the above information although all these metal ions are accessible to aromatics on the basis of FTIR results.

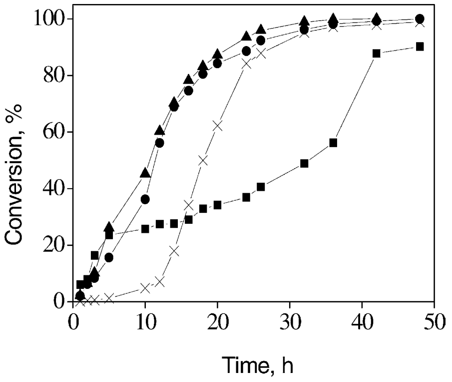

Fig. 6. Variation of the styrene conversion as a function of reaction time (h). VTi-1 and NbTi-1: the defined amount of H_2O_2 was introduced at the beginning of the reaction and VTi-2 and NbTi-2: the defined amount of H_2O_2 was divided in different portions and introduced step by step ((×) VTi-1, (●) VTi-2, (■) NbTi-1, (▲) NbTi-2).

Fig. 6 depicts the variation in styrene conversion as a function of reaction time while Fig. 7 reports the variation in reaction rate of the styrene oxidation as a function of reaction time using a series of catalysts.

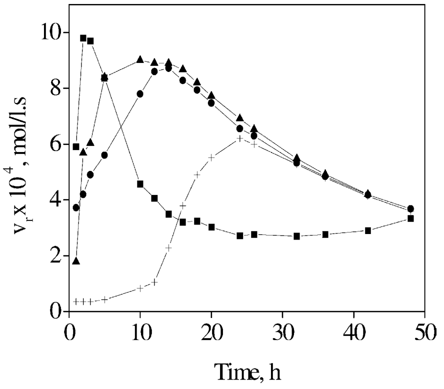

Fig. 7. Variation of the reaction rate as a function of reaction time (h). VTi-1 and NbTi-1: the defined amount of H_2O_2 was introduced at the beginning of the reaction and VTi-2 and NbTi-2: the defined amount of H_2O_2 was divided in different portions and introduced step by step ((×) VTi-1, (●) VTi-2, (■) NbTi-1, (▲) NbTi-2).

We present this series of results in two different ways to better evaluate the catalyst behavior with reaction time. Two injection modes of H_2O_2 have been investigated in order to find the optimal reaction conditions. From the first view, in oxidation of styrene, the conversion and selectivity to benzaldehyde of all the catalysts are very high after 20 h (Fig. 6). The catalytic behavior of NbTi under two different H_2O_2 injection conditions is quite similar while that of VTi is quite different. For conversion of styrene, the catalyst VTi-1 needs an induction period while VTi-2 and NbTi-1 and -2 convert styrene rapidly without this induction period. In summary of this part of results, compared to the situation where H_2O_2, catalyst and reagents were mixed at the beginning of the reaction (curves of VTi-1 and NbTi-1, Figs. 6 and 7), the introduction of the H_2O_2 step by step (curves NbTi-2 and VTi-2, Figs. 6 and 7) increases significantly the reaction rate in the first 10–20 h (Fig. 7) and decreases the selectivity of VTi catalyst. The rate of reaction reaches the maximum value only after 12 h reaction. We can see clearly that for NbTi catalyst, the mixture of H_2O_2 with reagents, solvent and catalyst at the beginning of reaction conducts to a very high initial and increasing reaction rate while after 5 h reaction, reaction rate decreases gradually (Fig. 7). It is evident that the behavior of VTiNS and NbTiNS catalysts under two reaction conditions is quite different. For NbTiNS catalyst, the initial rate is high when the total amount of H_2O_2 was added at the beginning of reaction. Why VTi-MCM-41 catalyst behaves differently when the introduction mode of H_2O_2 is different, at the moment it is not clear. More work has to be done to explain this interesting observation.

It is also observed that the conversion increases with temperature and hydrogen peroxide/styrene molar ratio. In Fig. 8, it can be seen a significant effect of the H_2O_2/styrene molar ratio on the conversion of styrene to benzaldehyde in the range 296–343 K.

It is interesting to note that with the catalysts modified by vanadium, the conversion of styrene and efficiency of H_2O_2 increase in the absence of acetonitrile. While with the Nb-MCM-41 and NbTi-MCM-41, in absence of the solvent, the rate of polymerization of styrene is higher than that of its oxidation to benzaldehyde.

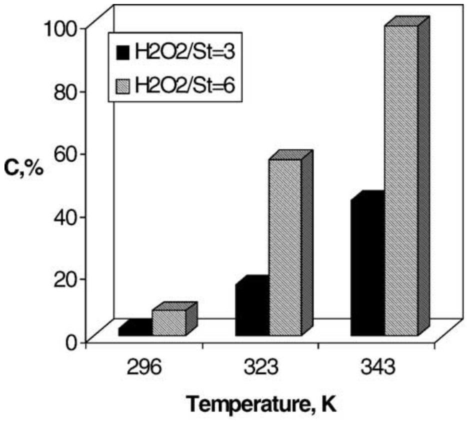

Fig. 8. Influence of the temperature and H_2O_2/styrene molar ratio on the conversion of styrene.

The conversion of alcohols to aldehydes on V-modified MCM-41 samples was also realized and showed to be very low and increased in the order: hexanol < cyclohexanol < hexanediol. Used V-MCM-41 molecular sieves after alcohols oxidation have been characterized by XRD, TEM and SEM techniques and show a less-ordered structure. 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.

4. Conclusions

V-, Nb-MCM-41 mesoporous molecular sieves and their further modification by Ti prepared by direct synthesis have an ordered hexagonal structure confirmed by the XRD, TEM, SEM and N_2 adsorption–desorption. Vanadium-containing catalysts are more active in hydroxylation of benzene and toluene and niobium-containing catalysts have a high activity in oxidation of styrene to benzene. The V-MCM-41 and Nb-MCM-41 catalysts obtained from TEOS, have a higher selectivity than the same catalysts prepared from sodium silicate. All the V-modified MCM-41 samples show very low activity in oxidation of alcohols.

The presence of titanium in the V- and Nb-MCM-41 catalysts can strongly modify their activity and selectivity in oxidation of aromatic hydrocarbons. The activity of the catalysts can also be influenced by the reaction conditions such as temperature and molar ratio of the reactants.

The reaction rate and selectivity in oxidation of styrene was modified by the introduction mode of the H_2O_2 into reaction medium, an induction period is needed for VTi-1 catalyst in oxidation of styrene when the oxidant, reagent, catalyst and solvent are mixed together at the beginning of the reaction.

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