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Activity and stability of bimetallic Co (V, Nb, La)-modified MCM-41 catalysts

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Abstract

A series of bimetallic mesostructured Co (V, Nb, La)-MCM-41 molecular sieves with high surface area and narrow pore-size distribution were obtained by direct hydrothermal synthesis using two different silica sources. Their catalytic activity was tested in the oxidation of styrene and benzene with hydrogen peroxide. Structural and textural properties of the fresh and used catalysts were studied by X-ray powder diffraction, nitrogen adsorption–desorption, TEM and SEM. The influence of the synthesis procedure, composition and metals molar ratio on the structure, catalytic activity and selectivity was discussed. The activity of bimetallic catalysts was compared with that of monometallic Co-, V-, Nb- and La-MCM-41 molecular sieves. It was found that more ordered hexagonal structure favors the selectivity to benzaldehyde and decreases the induction time of reaction. The introduction of V as the second metal ions into Co-MCM-41 decreases or increases sharply the activity in the oxidation of styrene and benzene, respectively. While the introduction of Nb showed an opposite tendency, suggesting that the combination of Co-V favors the oxidation of styrene and Co-Nb the oxidation of benzene and that the catalytic sites for oxidation of styrene and benzene are different. No benefic effect has been observed by incorporation of La into Co-MCM-41 neither in oxidation of styrene nor in oxidation of benzene. It was found that the benzaldehyde formation is structure sensitive.

Keywords: Bimetallic molecular sieves; CoV-MCM-41; CoNb-MCM-41; CoLa-MCM-41; Hydrocarbon oxidation; Hydrogen peroxide

1. Introduction

Molecular sieves containing small amount of catalytically active transition metals showed remarkable activity in selective oxidation of the organic compounds with hydrogen peroxide under mild conditions [1–4]. These properties result from the high dispersion of the metal ions as isolated species on the support with an ordered structure and pore dimensions. The metal ions can be introduced into molecular sieves in two different ways: ion exchange [5,6] and direct synthesis [7–11]. In any case, Me^{n+} in different coordination geometries and positions (surface, lattice) can simultaneously be present [12,13].

Cobalt, vanadium, niobium and lanthanum are interesting transition-metal ions in oxidation of organic compounds. The studies realized on the cobalt or vanadium-containing mesoporous molecular sieves had shown small distortion of the tetrahedral, after substitution of Si by the metal atoms in lattice, and the possibility of the oxidation of Co^{2+} and V^{4+} to Co^{3+} and V^{5+}, respectively [12,14]. These properties depend on the support structure. A higher distortion of the hexagonal MCM-41 structure was evidenced for La-MCM-41 molecular sieves [15]. It was also shown that La may improve the thermal and hydrothermal stabilities of Si-MCM-41 molecular sieves. This behavior can be the results of La^{3+} ions coordination [16]. In the viewpoint of catalytic activity, some of these metal ions gave a high catalytic conversion but low selectivity, others led to the inverse results.

The incorporation of two different metals might therefore create materials with different or new redox and acid properties [15,17]. This can combine the high activity of some metal ions and the high selectivity of others in aromatics oxidation. However, only a few studies concern the synthesis and catalysis of bimetallic ions modified mesoporous molecular sieves [18–26]. Recently, we have reported that the incorporation of metal ions was favored with sodium silicate as silica source while a less well ordered structure was obtained and the TMOS as silica source led to a well

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ordered structure but less incorporation of metal ions [18]. The synthesis method can also influence the activity of the metal containing MCM-41 catalyst and rate of the oxidation reaction [19]. In the present paper, the bimetallic Co (V, Nb and La)-MCM-41 molecular sieves were prepared by direct synthesis using two silica sources, sodium silicate and TEOS. The fresh catalysts have comprehensively been characterized and tested in oxidation of aromatic hydrocarbons in liquid phase. We would like to study the effect of two metal ions and to try to shed some lights on the role of each metal ion in the oxidation of aromatics.

2. Experimental

2.1. Synthesis

Bimetallic mesostructured Co (V, Nb, La)-MCM-41 molecular sieves with high surface area and narrow pore-size distribution were obtained by direct hydrothermal synthesis using two synthesis procedures differing in the silica precursors.

The metal sources were $Co(NO_3)_2\cdot 6H_2O$, $VOSO_4\cdot 5H_2O$, $NbCl_5$ and $La(NO_3)_3\cdot 6H_2O$. The cethyltrimethylammonium bromide (CTMABr) was used as surfactant, tetramethylammonium hydroxide (TMAOH), as base and electrolyte, ethanol, 2-propanol and water as solvents. Niobium was stabilized with oxalic acid [23].

2.1.1. S series of catalysts

Sodium silicate was used as silica source. The hydrothermal synthesis was carried out using gels with the molar composition of 1.0 SiO_2:xM^{n+}:0.48 CTMABr:0.28 Na_2O:3.7 TMAOH:222 H_2O.

2.1.2. T series of catalysts

The silica source was TEOS and the molar composition of the gel was 1.0 SiO_2:xM^{n+}:0.2 CTMABr:0.07 H_2SO_4:6.5 EtOH:1.0 2-PrOH:96 H_2O.

The gels obtained were then loaded into Teflon link steel autoclave and heated at 373 K for 3 days. For T series of catalysts, after this treatment the pH was adjusted to 11 and hydrothermal treatment was continued for another 3 days at the same temperature.

For both methods, $x = 0.04$, and the molar ratio of Co/Nb and Co/La was fixed at 1. Co/V molar ratio was varied between 0.3 and 3 (0.3 for VCo1-MCM-41, 1 for VCo2-MCM-41 and 3 for VCo3-MCM-41). For comparison, mono metallic ions (Co, V, Nb, La)-MCM-41 samples ($x = 0.02$) were prepared. The products obtained were filtered, washed, dried at 373 K and calcined in a flow of N_2 and then air at 773 K (823 K for the samples with La).

2.2. Characterization

Structural and textural properties of the materials obtained were studied by X-ray powder diffraction (Philips PW 170 diffractometer), nitrogen adsorption–desorption (Tristar), scanning electron microscopy (SEM) with a Philips XL-20 microscope and transmission electron microscopy (TEM) with Philips Tecnai microscope. Concentration of the metals was obtained by atomic adsorption (TJA Solar 969A spectrometer).

2.3. Catalytic experiments

Oxidation reactions were carried out for 12–48 h in a temperature range of 203–343 K under stirring in the presence or absence of the solvent (acetonitrile). The molar ratio of hydrocarbon/solvent/hydrogen peroxide was 1/–/3 for benzene and 1/1.8/3 for styrene. After separation of the catalyst by centrifugation, the analyses of the oxidation products were 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 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. The used catalysts were characterized by TEM, SEM and FTIR.

3. Results and discussion

3.1. Catalysts characterization

The powder XRD patterns of bimetallic molecular sieves synthesized from TEOS (T series) reflect a typical well-defined MCM-41 structure while the less ordered structure is evidenced for the S series of samples obtained from sodium silicate (Fig. 1).

The higher values of the unit cell parameter a_0 of S series of samples than that of pure siliceous MCM-41 ($a_0 = 4.3$ nm) can be taken as an indication of the incorporation of the metals in the silica framework (Table 1). These results combined with the well resolved XRD patterns and the lower unit cell parameters of T series of samples are in accordance

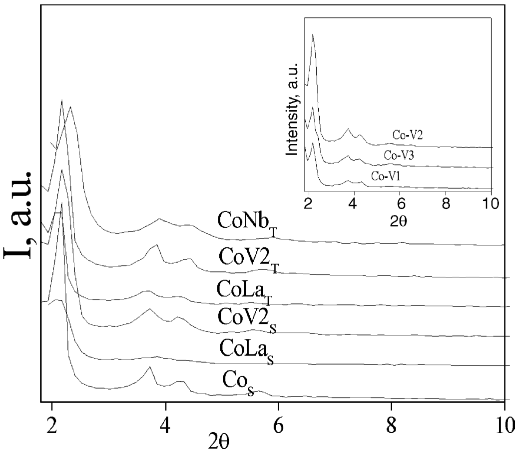

Fig. 1. X-ray diffraction patterns of the samples.

Table 1
Characteristics of the samples

Sample	a_0 (nm)	S_{BET} (m^2/g)	$Ø_{BJH}$ (nm)	Sample	a_0 (nm)	S_{BET} (m^2/g)	$Ø_{BJH}$ (nm)
CoV1$_S$	4.7	948	2.8	CoLa$_T$	4.2	902	2.8
CoV2$_S$	4.6	1013	2.7	Co$_S$	4.6	990	2.8
CoV3$_S$	4.7	973	2.8	V$_S$	4.6	965	2.9
CoV2$_T$	4.3	1146	2.8	V$_T$	4.5	1032	2.8
CoNb$_s$	–	568	5.5	Nb$_S$	3.9	842	2.5
CoNb$_T$	3.7	874	2.9	Nb$_T$	3.8	912	2.8
CoLa$_S$	4.2	760	2.9	La$_S$	4.6	815	2.8

with our recent results that TEOS favors the formation of hexagonally organized mesochannels while sodium silicate facilitates the incorporation of metal ions into the framework and provokes a disorganization of mesostructure [18]. A very surprising observation that the unit cell parameter (a_0) of all the Nb-containing MCM-41 mesoporous molecular sieves are particularly low. At the moment, no any explanation was emitted. A framework contraction caused by the substitution of Si by Nb could be the origin of this decrease in unit cell parameter. Table 2 gives the content of metal ions in all the studied samples. The amorphous structure of NbCo$_S$ sample could be due to the large amount of metals incorporated into the silica framework.

TEM images of the bimetallic mesoporous molecular sieves (Fig. 2) are characteristics for the mesoporous materials with hexagonal channel array, showing high quality in organization of channels of these catalysts.

SEM pictures of bimetallic molecular sieves show the spherical morphology, typical for the mesoporous metallosilicates, and a higher dimension of the particles of S series of samples (Fig. 3) although some agglomerates are visible for T series of samples.

The general trend is that the specific surface area of all the metal-containing molecular sieves decreases compared with Si-MCM-41. Fig. 4 show the isotherms (A) and the pore size distributions (B) of a series of CoV-MCM-41 samples. The type IV isotherms of the samples with a different Co/V molar ratio are practically identical and are characterized by a steep increase at the relative pressure P/P_0 of 0.36, indicating the homogeneity of our bimetallic incorporated mesoporous molecular sieves. The BJH pore size distribution shows a narrow monomodal peak centered at about 2.8 ± 0.2 nm for all the samples with hexagonal arrangement (Table 1).

Table 2
Composition and catalytic activity of S and T series of catalysts in oxidation of styrene

Sample	Metal content (%)		$C_{styrene}$ (%)	$S_{benzaldehyde}$ (%)
	M_1	M_2		
Co$_S$	1.84	–	21.3	92.4
CoV1$_S$	0.78	2.45	2.3	98.4
CoV2$_S$	1.86	1.58	3.8	94.6
CoV3$_S$	2.82	0.80	24.5	94.4
CoNb$_S$	1.88	2.92	96.4	73.7
CoNb$_T$	1.85	2.94	49.2	99.2
CoV2$_T$	1.87	1.60	2.8	96.2
CoLa$_S$	1.84	4.35	1.8	94.5
CoLa$_T$	1.84	4.36	1.6	98.2

Reaction conditions: $m_{cat} = 70$ mg, reaction time and temperature 24 h at 343 K.

In accordance with XRD results, the mesoporous sieves synthesized from TEOS are typically MCM-41 materials with a high surface area and pore volume. CoNb samples obtained from sodium silicate show a structural disorganization and have lower surface area and the pore volume. Compared with the Nb$_T$ sample, the surface area of NbCo$_T$ samples decreases slightly. Drop in the surface area is more significant for the samples containing niobium or lanthanum. These results are in agreement with XRD patterns (Fig. 1) and variation of $R_{Mn^+}/R_{O^{2-}}$ ratio. The possibility of a tetrahedral geometry for these transition metal ions increases in order of La^{3+} < Nb^{5+} < Co^{2+} < V^{5+}.

3.2. Catalytic activity

The catalytic properties of calcined bimetallic molecular sieves were examined by carrying out the oxidation of styrene and benzene with H_2O_2 as test reaction. Monometallic Co-, V-, Nb- and La-MCM-41 catalysts were evaluated for comparison under similar conditions to study the effect of second metal ions on the activity and selectivity of catalysts.

Bimetallic molecular sieves are active in oxidation of styrene with H_2O_2. The obtained conversion of styrene on S series of catalysts is higher compared with that of T series of catalysts. For all the catalysts the increase in reaction temperature favors the conversion of styrene in oxidation reaction (Fig. 5).

Effect of the second metal on the properties of Co-MCM-41 catalysts was evidenced. Firstly, the introduction of V and La reduces sharply the conversion of styrene (Table 2), but with increasing Co/V molar ratio (decreasing V amount), the catalytic activity increases (Fig. 6 and Table 2). The highest conversion is obtained with the Co/V molar ratio of 3.0 after 48 h of reaction (Fig. 6).

On the other hand, the effect of the second metal on the reactivity is different for each aromatic hydrocarbon. The introduction of V or Nb into Co-MCM-41 molecular sieves decreases or increases the conversion of styrene, respectively. While the opposite tendency is observed (Fig. 7) that

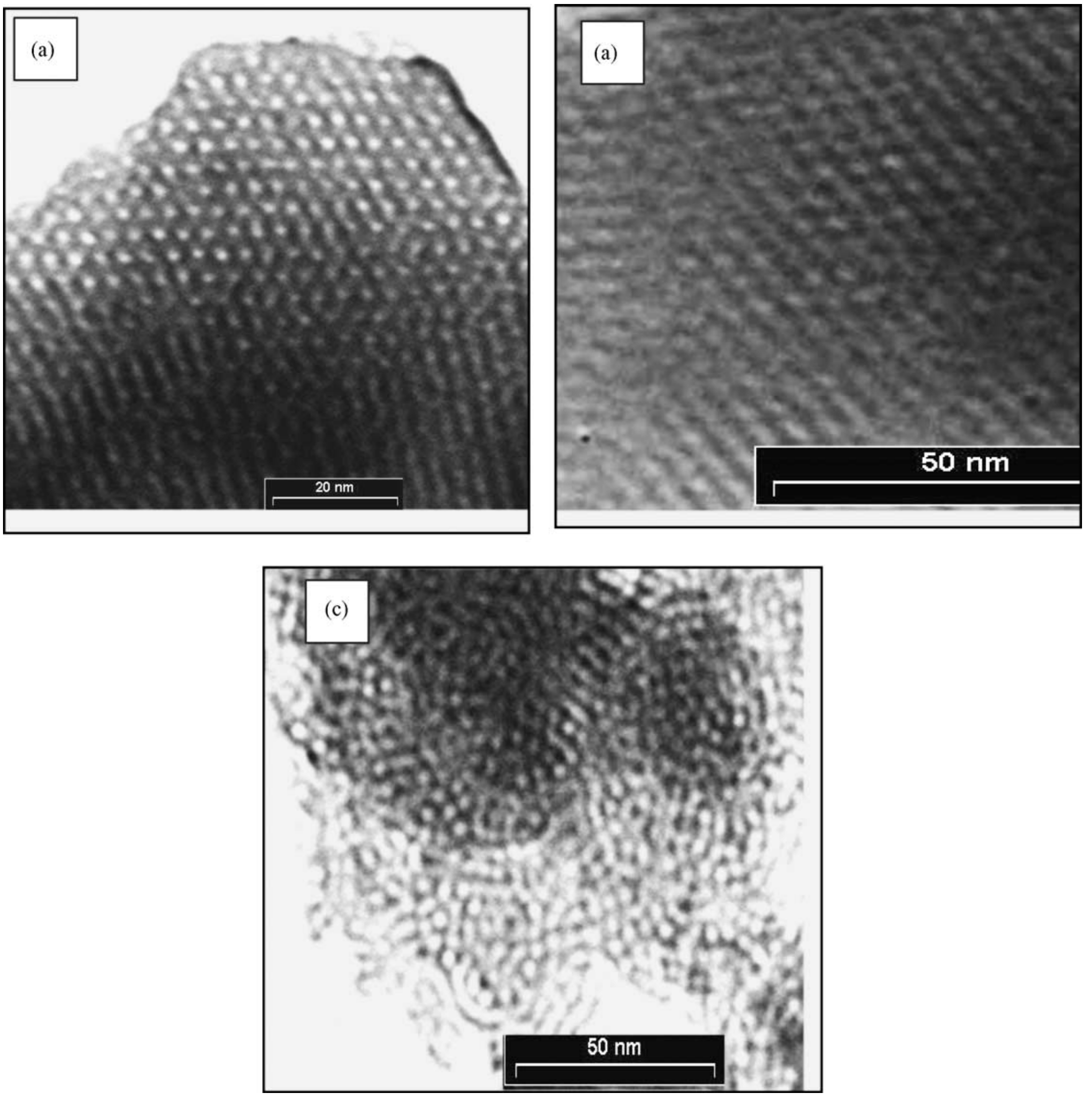

Fig. 2. TEM images of $CoV1_S$ (a), $CoNb_T$ (b) and $CoLa_S$ (c) -MCM-41 molecular sieves.

the combination of Co with V or Nb increases or decreases, respectively, the catalytic activity in oxidation of benzene. The effect of introduction of La into Co-MCM-41 is quite surprising since the activity for oxidation of styrene and benzene decreases, implying the inhibition effect of La for oxidation of aromatics.

The main reaction products are benzaldehyde for oxidation of styrene and phenol for oxidation of benzene. The more ordered hexagonal structure, for example $CoNb_T$ (compared with $CoNb_S$) favors the selectivity to benzaldehyde, showing the structure sensitivity of benzaldehyde formation. For all the catalysts is necessary an induction period at the beginning of the reaction since the activity is lower initially but increases after 12–24 h reaction.

After first utilization the separated and dried catalysts were reused. The catalytic activity of these reused catalysts increases but then decreases after third utilization. It is observed that the selectivity decreases gradually with reaction time and further decreases in second utilization. Some polycondensed products due to the polymerization of formaldehyde and/or benzaldehyde were detected after long time of reaction, a possible reason for decrease in selectivity with reaction time. For bimetallic samples containing V ions, a slight leaching was observed, but for others, the leaching is insignificant.

3.3. *Characterization of used catalysts*

TEM images of the used catalysts show a well ordered structure with hexagonal arrangement of channels, indicating no effect of the reaction on the catalyst structure after first and second reaction (Fig. 8). This observation confirms the good stability of bimetallic molecular sieves.

The IR study of adsorbed phase in discharged catalysts after first cycle reaction of styrene and benzene upon desorption at a series of temperatures (293, 373, 623 and

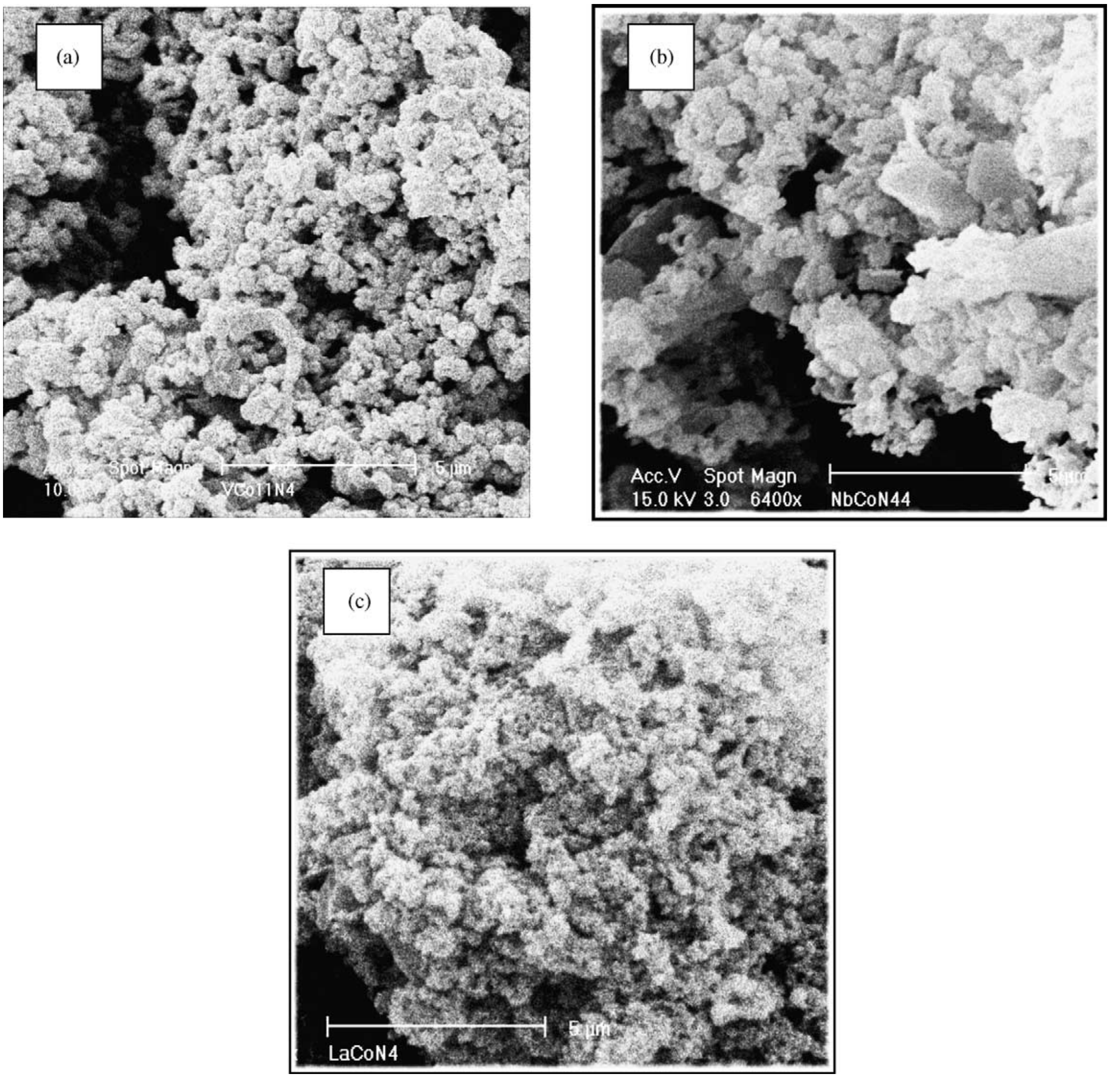

Fig. 3. SEM images of the $CoV2_S$ (a), $CoNb_S$ (b) and $CoLa_S$ (c) -MCM-41 samples obtained from sodium silicate.

723 K) was made. The presence of different aromatic species such as benzaldehyde and styrene glycol was noted. These species adsorbed very strongly in the catalyst since a complete desorption of these species can be made only after a desorption at 723 K. The strong adsorption of these species was confirmed by thermal analysis. The observation of these species can be helpful in understanding the reaction mechanism.

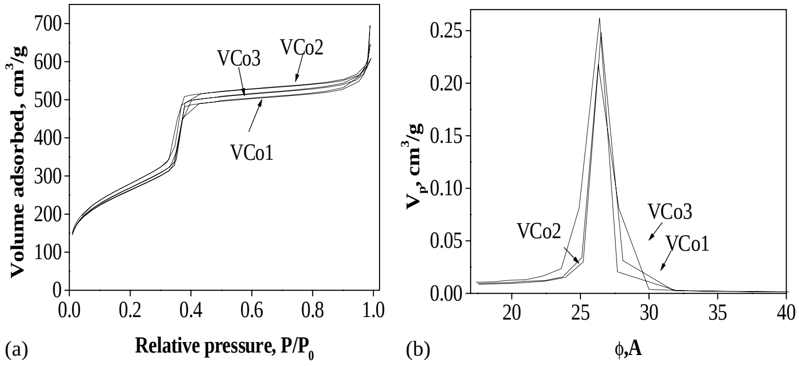

Fig. 4. N_2 adsorption–desorption isotherms (A) and pore size distribution (B) of a series of V-Co/MCM-41 samples.

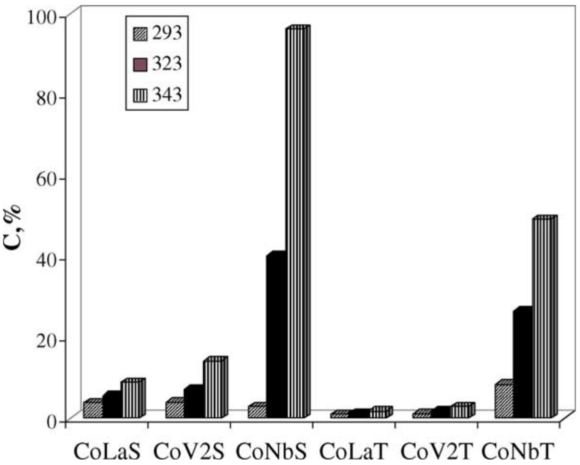

Fig. 5. Conversion of styrene for S and T series of bimetallic catalysts as a function of reaction temperature (K) (molar ratio $M_1/M_2 = 1$; reaction time: 48 h; amount of catalyst: 70 mg).

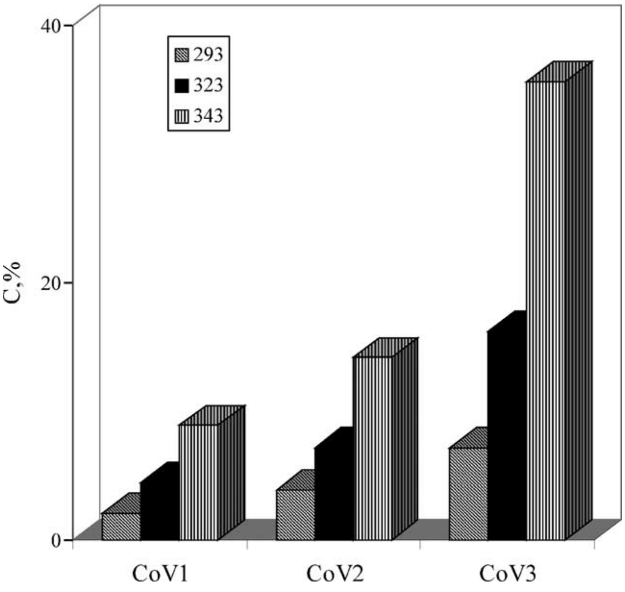

Fig. 6. Conversion of styrene for various CoV-MCM-41 catalysts as a function of reaction temperature (K) (reaction time: 48 h; amount of catalyst: 70 mg).

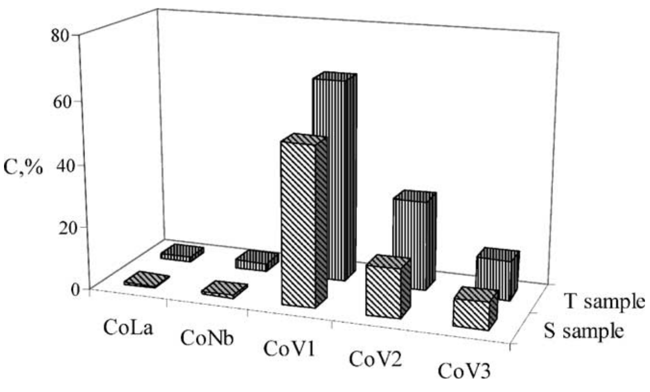

Fig. 7. Conversion of benzene for S and T series of bimetallic catalysts (reaction time: 24 h; temperature: 343 K; amount of catalyst: 70 mg).

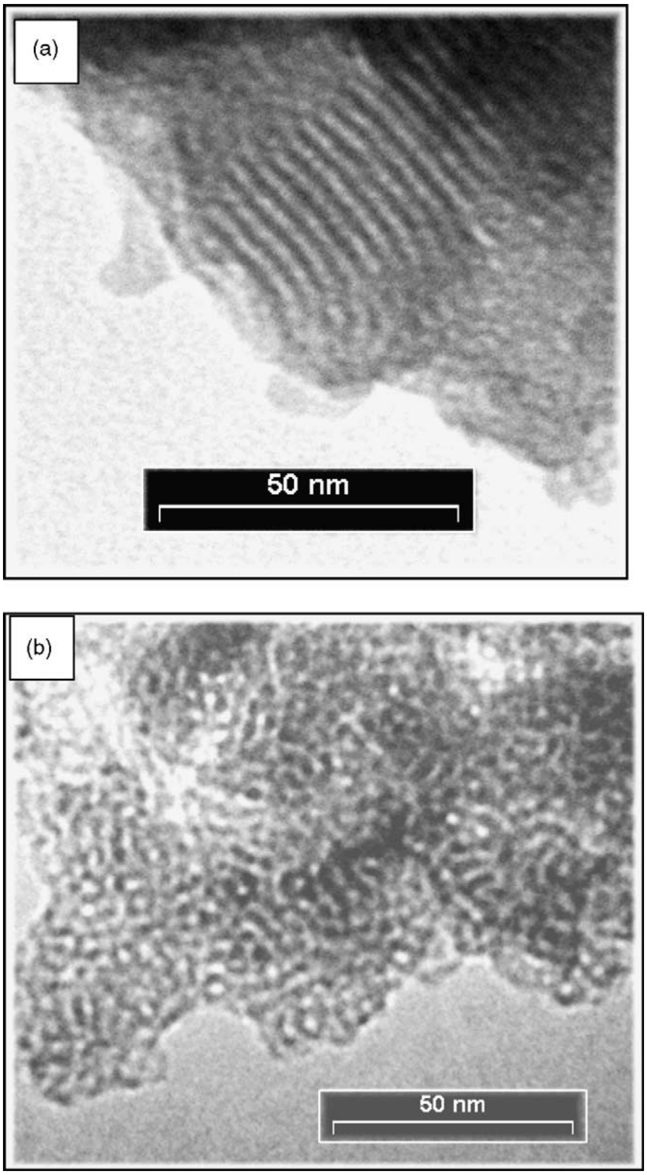

Fig. 8. TEM images of CoV1-MCM-41 (a) and CoLa-MCM-41 (b) molecular sieves after second utilization.

4. Conclusions

Bimetallic molecular sieves with ordered hexagonal structure have been obtained by direct synthesis from two different silica precursors. The results show that using sodium silicate as silica source the metal ions are more easily incorporated in the framework, but provoking a disorganization of mesostructure for CoNb- and CoLa-MCM molecular sieves. All the samples synthesized with TEOS have a well organized mesostructure and a smaller unit cell parameter as a consequence of less incorporation metal ions into the framework. A high conversion of styrene was obtained on CoNb catalysts and a high conversion of benzene was obtained on CoV catalysts, especially prepared by using TEOS. The more ordered hexagonal structure favors the selectivity to benzaldehyde and decreases the induction time of reaction.

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