



Liquid phase oxidation of aromatic hydrocarbons using highly ordered Nb and NbCo-MCM-41 nanoreactors

V. Parvulescu¹, C. Constantin², B.L. Su*

*Laboratoire de Chimie des Matériaux Inorganiques, ISIS, The University of Namur (FUNDP),
61 rue de Bruxelles, B-5000 Namur, Belgium*

Received 12 September 2002; accepted 27 February 2003

Abstract

A series of Nb- and NbCo-containing mesoporous catalysts with variable Nb/Si molar ratios and a highly ordered hexagonal arrangement of the pores have been hydrothermally synthesized from sodium silicate or tetraethylortosilicate. The prepared materials were characterized by various techniques, such as: X-ray diffraction (XRD), N₂ adsorption–desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The oxidizing character of the Nb- or NbCo-MCM-41 materials was revealed in the selective oxidation of styrene, benzene and toluene with H₂O₂ in liquid phase. A kinetic study was realized for oxidation of styrene with Nb-MCM-41 catalysts. All the Nb and NbCo modified mesoporous catalysts were very active in oxidation of styrene with H₂O₂.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Niobium; Niobium-cobalt; Modified MCM-41; Synthesis; Hydrocarbons oxidation; Hydrogen peroxide

1. Introduction

The activity of niobium compounds as acid, selective oxidation and photosensitive catalysts is really remarkable [1–3]. Depending on the catalyst composition and structure, they are used in the processes involving acidic centers as well as redox characters. Niobium modified molecular sieves are a new class of materials with catalytic properties in NO decomposition, reduction of NO with NH₃, hydrosulphurization of methanol [4,5] and catalytic oxidation

of sulphides [6], cyclohexene [7], alcohols [8] and thioethers [5] with hydrogen peroxide. Nb-MCM-41 mesoporous sieves have shown to be not only more active in oxidation reactions with H₂O₂ but also more stable than V- or Ti-containing samples since Ziolk et al. [5] have reported no leaching of metal species from Nb-MCM-41 solid during the reaction with H₂O₂.

Niobium modified mesoporous silicates obtained by direct synthesis [4,5] or impregnation [5] can contain Nb species in extra-framework portion or in skeleton of the molecular sieves. Niobium oxide species [NbO_n^{(5–2n)+}] [5], which occupy the extra-framework cation position, can play the role of the acid sites and exhibit redox properties. Niobium ions incorporated in the framework of the mesoporous MCM-41 molecular sieves provokes equally Lewis acidity and oxidizing properties. The acidity of the

* Corresponding author. Tel.: +32-81-72-45-31;
fax: +32-81-72-54-14.

E-mail address: bao-lian.su@fundp.ac.be (B.L. Su).

¹ On leave from Institute of Physical Chemistry “I.G. Murgulescu”, Spl. Independentei 202, Bucharest, Romania.

² On leave from CMMM, Spl. Independentei 204, Bucharest, Romania.

transition metal ion-containing MCM-41 molecular sieves was evidenced by IR spectroscopy upon ammonia, benzene or lutidine adsorption [5,9,10] and was assigned to Brønsted acid sites (surface hydroxyl groups) and Lewis acid sites arising from coordinated metal in the framework. Considering oxo-metal ($X-M=O$) or peroxy-metal species as active sites in oxidation reactions, their oxidizing power can increase by combinations with the Lewis acidity.

In this paper, we describe the preparation and characterization of highly ordered Nb and NbCo-MCM-41 molecular sieves. By comparing samples synthesized from sodium silicate and TEOS as silica sources we demonstrate effects of the preparation on the porous structure, morphology and catalytic properties. The catalytic activity was determined in oxidation of styrene, benzene and toluene with hydrogen peroxide.

2. Experimental

2.1. Synthesis

Nb and Nb-Co were incorporated into the mesoporous MCM-41 molecular sieves by direct synthesis using two different methods differing in the silica precursors. The niobium and cobalt sources were $NbCl_5$ and $Co(NO_3)_2 \cdot 6H_2O$, respectively. 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 [4].

2.1.1. Method I

Silica source was sodium silicate and the hydrothermal synthesis was carried out using gels with the following molar composition: $1.0SiO_2 : xM^{n+} : 0.48CTMABr : 0.28Na_2O : 3.7TMAOH : 222H_2O$. A defined amount of alcoholic (2-propanol) $NbCl_5$ solution was introduced, by dropwise, in aqueous acid oxalic solution. The obtained solution was added under stirring to a mixture of 3.8 g sodium silicate, 2.8 g CTMABr and 30 g H_2O . After 2 h stirring, TMAOH solution was added. The gels obtained was sealed into Teflon-lined steel autoclaves and heated at 373 K for 5 days. The pH value was adjusted to 11 with H_2SO_4 .

2.1.2. Method II

Tetraethylortosilicate (TEOS) was used as silica source, and the molar composition of the gel was: $1.0SiO_2 : xM^{n+} : 0.2CTMABr : 0.07H_2SO_4 : 6.5EtOH : 1.02PrOH : 96H_2O$. The solution of alcoholic $NbCl_5$ and oxalic acid, prepared in the same manner as in the first method, was added to the mixture of TEOS, ethanol and CTMABr. The pH was increased to 13 with NaOH solution (3 N). For both methods, $x = 0.02$ and 0.04 for Nb and 0.04 for NbCo-MCM-41 were used and the molar ratio Nb/Co was 1. The gels obtained in the second method 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 for another 3 days at the same temperature. The products obtained were filtered, washed, dried at 373 K and calcined in a flow of N_2 and then air at 773 K.

2.2. Characterization

The obtained materials were intensively 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 and Fourier transform infrared spectroscopy (FTIR) (Spectrum 2000, Perkin-Elmer). After reaction, the catalysts were further characterized by above techniques to study the stability of catalysts.

2.3. Catalytic experiments

Oxidation reactions were carried out under stirring in the presence or absence of the solvent (acetone-trile). The reaction temperature and time varied from 293 to 343 K and from 0 to 48 h, respectively. The molar ratio of hydrocarbon/solvent/hydrogen peroxide was 1/–/3 for benzene and toluene and 1/1.8/3 for styrene. A kinetic study was realized for oxidation of styrene with Nb-MCM-41 catalysts. After reaction, the catalyst was separated from reaction mixture 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. Catalyst active component leaching during the reaction was verified by resubmission of filtrates to reaction conditions.

3. Results and discussion

3.1. Multitechnique characterization of metal ions modified mesoporous catalysts

The powder XRD patterns of niobium-containing mesoporous samples synthesized from TEOS (NbT and NbCoT) exhibit four sharp diffraction peaks in the low angle region of $2\text{--}10^\circ$ (2θ), corresponding to the reflection lines of 100, 110, 200 and 210 and reflecting a typical well-defined MCM-41 structure (Fig. 1). While the less ordered structure is evidenced for the niobium modified materials obtained from sodium silicate (NbS1, 2.8% Nb and NbS2, 5.6% Nb), indicating that TEOS as silica source favors in the present case the better organization of mesoporous structure. This is quite in accordance with our very recent results that TEOS favors the well organization of mesostructure while sodium silicate favors the incorporation of metal ions into the framework and provokes a disorganization of mesostructure. Combining the present and our very recent results, we can conclude that the order of the hexagonal arranged pores depends strongly on the synthesis method (silica precursors, pH value of the gels, metal content and chemical state of metal ions)

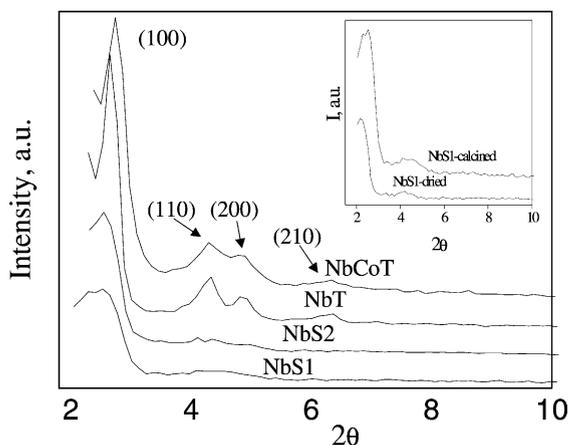


Fig. 1. X-ray diffractograms of a series of Nb- and NbCo-MCM-41 mesoporous molecular sieves.

[11,12]. The influence of the metal content on the hexagonal structure is insignificant. However, it is observed that the unit cell parameter increases with metal content for the samples synthesized from sodium silicate (3.89 nm for NbS1 and 4.12 nm for NbS2), indicating the incorporation of more metal ions in the framework in NbS2 sample since Nb–O bond length is larger than that of Si–O and the unit cell expansion is often used as a direct proof of the incorporation of metal ions in the lattice when the synthesis conditions remain identical. XRD patterns of as-synthesized and air-dried NbS1 samples are shown in the inserted frame of Fig. 1. The increase of the XRD signal intensity after calcination indicates the improvement in regularity of the structure. Upon calcination, the diffraction lines are shifted to higher 2θ values, for example, for 100 reflection line, it varies from 2.30 ($d_{100} = 3.85$ nm) to 2.62 ($d_{100} = 3.38$ nm), indicating a lattice contraction. The increase in regularity of structure accompanied by the contraction of the unit cell may suggest that some metal ions are removed from the framework upon calcination. A shift to higher 2θ values is evidenced for the NbT compared with the NbS samples with similar metal content introduced in the synthesis gel, corresponding to a decrease of the unit cell parameter (a_0), suggesting that less Nb ions are incorporated into the silica framework.

XRD results show clearly that using sodium silicate as silica source, Nb ions are really incorporated in the framework, provoking a disorganization of mesostructure. The calcination can remove some Nb ions from framework, leading to a contraction of unit cell. The calcined samples (which are used in oxidation reaction) contain therefore framework and extra-framework Nb ions. Concerning the samples synthesized with TEOS, less Nb ions are incorporated into the framework, a well organized mesostructure and a small unit cell parameter are obtained. These results are very important in explaining the catalytic properties of the samples.

NbCo sample obtained by method I using sodium silicate as silica source was amorphous while NbCo sample prepared with TEOS shows a quite well organized pore system. This confirms once again the role of TEOS in the synthesis of well ordered mesoporous materials. The very small unit cell parameter observed for this sample suggests the low metal content in the framework. The amorphous structure of NbCoS

Table 1

Characteristics of the Nb-MCM-41 and NbCo-MCM-41 samples and their activity in oxidation of the organic compounds

Sample	a_0 (nm)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	ϕ_{BJH} (nm)	Styrene		Benzene		Toluene	
				C (%)	S_{Bzald} (%)	C (%)	S_{Ph} (%)	C (%)	S_{Bzaldol} (%)
NbS1	3.89	842	2.5	87.2	18.4	10.9	86.4	3.1	98.4
NbS2	4.12	732	2.7	76.6	24.5	19.4	84.5	0.8	98.8
NbT	3.80	912	2.8	86.6	98.5	1.2	89.6	1.8	94.5
NbCoS	–	568	5.5	96.4	73.7	0.9	78.6	0.8	100
NbCoT	3.70	874	2.9	49.2	99.2	2.6	96.6	1.0	98.5

Reaction conditions: catalysts, 70 mg; molar ratio of organic compound/solvent/ $\text{H}_2\text{O}_2 = 1/1.8/3$ (styrene); $1/-/3$ (benzene and toluene); reaction temperature and time are 343 K and 48 h, respectively; a_0 , unit cell parameter; ϕ_{BJH} , pore diameter determined by BJH method using adsorption branch of isotherm; C (%), conversion of aromatics; S (%), selectivity of one product (benzaldehyde for styrene, phenol for benzene and benzalcohol for toluene).

sample synthesized with sodium silicate could be due to the large amount of metals incorporated into the silica framework. The surprising catalytic behavior of this sample which will be discussed in the following section seems to indicate the high metal content in the amorphous silica framework.

The N_2 adsorption–desorption isotherms of all mono- or bimetallic modified samples (except NbCoS sample) (not shown here) exhibit a sharp inflection at a relative pressure of about 0.36, characteristic of capillary condensation in uniform mesopores. In accordance with XRD results, niobium incorporated mesoporous sieves are typically MCM-41 materials with a high surface area and pore volume. However, it has to indicate that the samples synthesized from TEOS have higher surface area and pore volume than those from sodium silicate. The BJH pore size

distribution indicates a narrow and monomodal peak centered at around 2.7 ± 0.2 nm for all the samples with hexagonal arrangement (Table 1). In comparison with the NbT sample, the surface area of NbCoT samples decreases slightly.

Transmission electron micrographs of NbS1, NbT and NbCoT samples are shown in Fig. 2. The ordered arrangement, typical for the MCM-41 materials, of all the samples is observed and confirms the results from the XRD characterization.

SEM pictures of the NbS1, NbT and NbCoT samples, given in Fig. 3, are typical for the mesoporous metallosilicates and show a morphology of spherical particles. The particle size of samples ranges from 400 to 700 nm. It is clearly visible that most of particles are almost perfectly spherical (NbS samples) although some agglomerates are detected (NbT and NbCoT

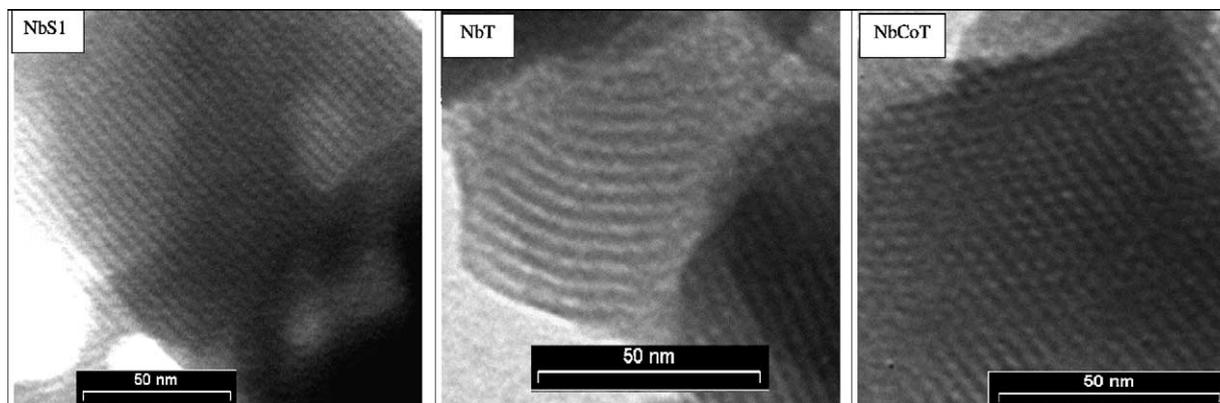


Fig. 2. TEM images of a series of Nb- and NbCo-modified MCM-41 samples.

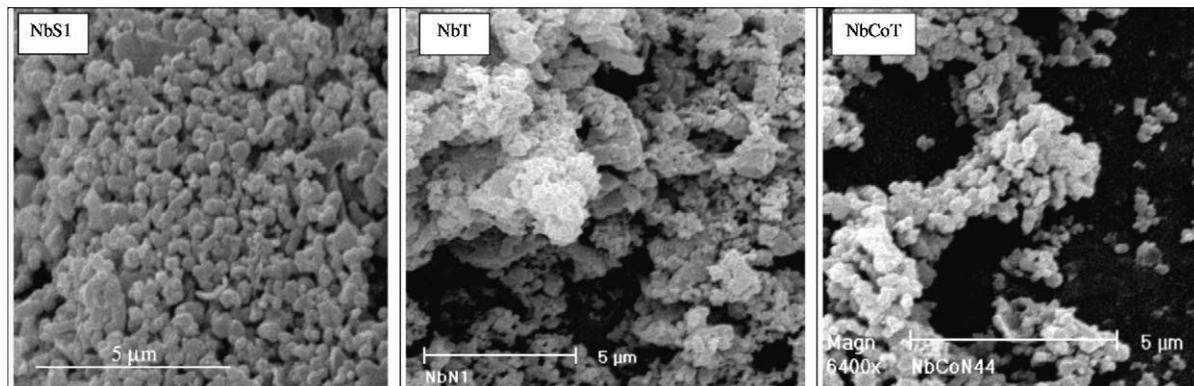


Fig. 3. SEM images of the Nb- and NbCo- modified MCM-41 samples.

samples). A higher dimension of the NbS1 particles is evidenced by the SEM images.

In the FTIR spectra of the calcined Nb-MCM-41 and NbCo-MCM-41 samples, the anti-symmetric and symmetric stretching vibration bands of framework Si–O–Si bonds appear at 1086 and 804 cm^{-1} , respectively (Fig. 4). The band associated with the asymmetric stretching frequency of framework Si–O–Si bonds shifts from 1086 cm^{-1} (NbS1) to 1076 cm^{-1} (NbS2). This may support the incorporation of niobium into the MCM-41 framework. In all samples, a IR band at around 960 cm^{-1} is also observed. Such a band has been assigned to a stretching vibration mode of a $[\text{SiO}_4]$ unit bonded to a niobium ion ($\text{O}_3\text{Si}-\text{O}-\text{NbO}_3$). However, the origin and interpretation of this band still remain controversial because this band is

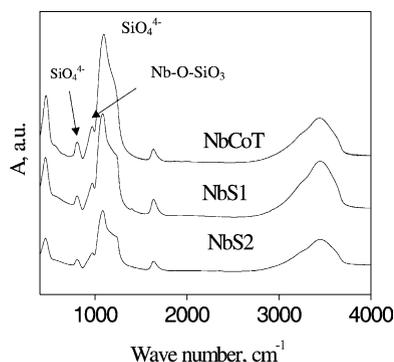


Fig. 4. FTIR spectra of the NbS2, NbS1 and NbCoT samples (sample powders are dispersed in KBr).

observed most prominent in the IR spectrum of calcined MCM-41 samples.

Combining the XRD and FTIR results, it is obvious that Nb ions are really incorporated into the silica framework, but calcination provokes the removal of Nb ions from the framework, especially for NbS samples. Therefore, in the calcined NbS samples which will be used as catalysts in oxidation reaction, two kinds of Nb species could be present, framework and extra-framework Nb species. We have to take into account the participation of these two kinds of Nb species in oxidation reaction.

3.2. Catalytic activity in oxidation of aromatics

The catalytic properties of calcined Nb- and NbCo-MCM-41 samples and NbCo amorphous solid were examined by carrying out the oxidation of aromatic hydrocarbons with H_2O_2 as test reaction (Table 1). The effect of reaction temperature has also been studied (Fig. 5). All the catalysts are very active in oxidation of styrene with H_2O_2 . While the activity is very low in oxidation of benzene and toluene. The obtained conversion of styrene on NbCoS catalyst is higher compared with that for NbCoT catalyst (Fig. 5 and Table 1). It is clear that the increase in reaction temperature favors the conversion of aromatics in oxidation reaction.

The main reaction products are benzaldehyde for oxidation of styrene, phenol for oxidation of benzene and benzalcohol for oxidation of toluene. The more ordered hexagonal structure favors the selectivity to

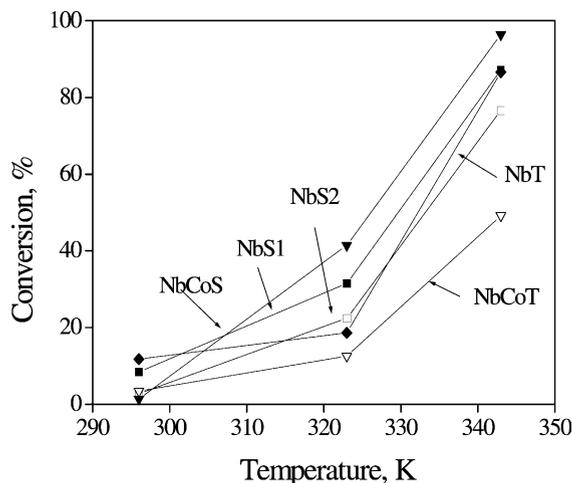


Fig. 5. Conversion in oxidation of styrene of a series of catalysts as a function of reaction temperature (reaction time is 48 h, amount of catalyst is 70 mg and styrene/solvent/ $\text{H}_2\text{O}_2 = 1/1.3/3$).

benzaldehyde or phenol for all the Nb-MCM-41 and NbCo-MCM-41 catalysts. An induction period at the beginning of the reaction for all the catalysts is necessary, but this period is not very long for NbS1 catalyst compared with NbT catalyst (Fig. 6). It seems that it depends on the metal content and metal accessibility. As we have discussed in Section 3.1, NbS samples contain more Nb ions in the framework and also the

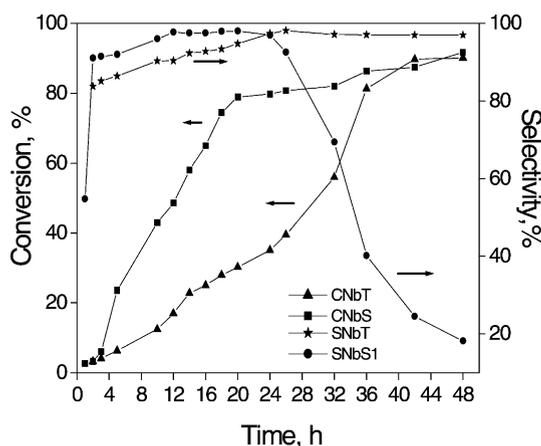


Fig. 6. Conversion and selectivity in oxidation of styrene of a series of catalysts as a function of reaction time (reaction temperature is 343 K, amount of catalyst is 70 mg and styrene/solvent/ $\text{H}_2\text{O}_2 = 1/1.3/3$).

extra-framework Nb ions. It is well known that both framework and extra-framework Nb ions are active in oxidation of hydrocarbons. The induction period observed with NbS catalysts in oxidation of styrene is therefore shorter since the extra-framework Nb ions are already available for the conversion of styrene at the beginning of reaction. However, NbT samples contain very low content of framework Nb ions. They are less accessible compared to those in extra-framework position. A longer induction period for conversion of styrene is thus needed. However, framework Nb ions are more selective for benzaldehyde formation. That is why very high selectivity is observed with NbT samples. Although the extra-framework Nb ions are active in oxidation of styrene, they are less selective compared with those located in the framework. More work has to be done to better explain this interesting observation. The average rate of reaction, between 5 and 26 h, is higher for NbS1 catalyst ($7.6 \times 10^{-4} \text{ mol l}^{-1} \text{ s}$) than NbT one ($2.8 \times 10^{-4} \text{ mol l}^{-1} \text{ s}$). A high conversion is obtained after 20 h of reaction for NbS1 catalyst while a simultaneous decrease in selectivity to benzaldehyde is also noted, indicating the further conversion of benzaldehyde to other products since a mixture of the polycondensed products was obtained after 24 h of reaction.

A high conversion is obtained after 16–24 h of reaction for all the catalysts. The activity of NbCoS sample is highest after 48 h reaction while the selectivity to benzaldehyde is lower for this amorphous NbCo catalyst. This is probably due to the fact that metal ions are very heterogeneously dispersed in the amorphous framework, thus no selectivity in conversion of styrene. However, they are still more selective than those located in the extra-framework position.

The variation of H_2O_2 efficiency (amount of H_2O_2 used in styrene oxidation/amount of H_2O_2 transformed) is similar for all the catalysts in the styrene oxidation reaction and the efficiency decreases with reaction temperature. H_2O_2 efficiency is even higher in the absence of the acetonitrile.

H_2O_2 is an aggressive oxidant and can leach metal cation from framework of mesoporous silicas. This was observed in V- [13], Co-, Fe- [9,10], and Ti-containing [5] mesoporous catalysts. However, it was reported that no metal leaching from Nb-MCM-41 and Ni-MCM-41 in oxidation reaction by using H_2O_2 as oxidant was detected. In the present work, leaching

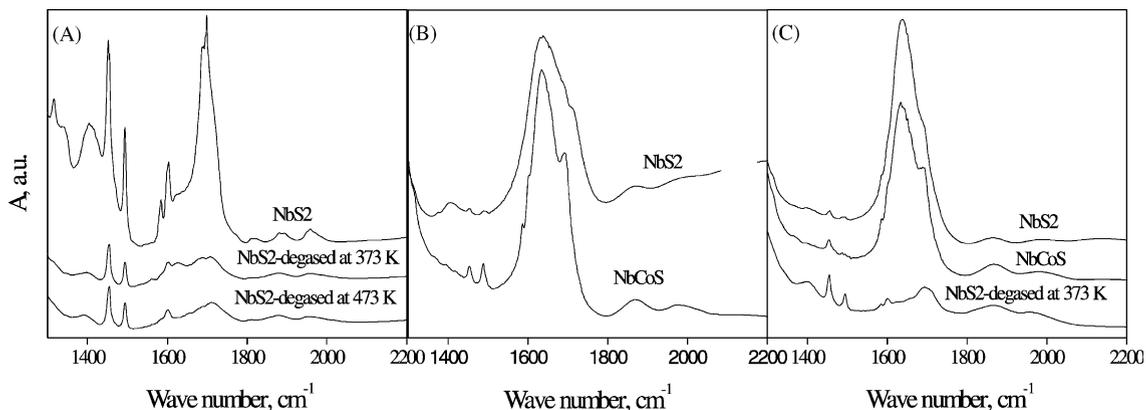


Fig. 7. FTIR spectra of adsorbed species in a series of catalysts after reaction of oxidation of styrene (A); benzene (B); and toluene (C) upon evacuation at different temperatures.

effect was also verified. For NbS samples, a slight leaching was observed. The Nb species in the liquid phase were from extra-framework. However, for NbT samples, no significant leaching was detected.

3.3. Characterization of used catalysts

TEM images of the used catalysts show an well ordered structure, indicating no effect of the reaction on the catalyst structure, confirming the good stability of Nb modified MCM-41 catalysts as observed previously [5,11]. SEM images of the used samples, compared with those of the catalysts after calcination show an effect of the reaction conditions on the morphology of the particle arrangement.

The IR spectra (Fig. 7) of Nb-MCM-41 catalyst after the reaction with styrene (A), benzene (B) and toluene (C) and after desorption at a series of temperatures (373 and 473 K) evidenced a strong adsorption of the aromatic species in the catalysts. A large number of vibration bands are observed from used samples after styrene oxidation reaction while only few vibration bands are visible from used samples after benzene (B) and toluene (C) oxidation reactions, confirming higher conversion of all the catalysts in oxidation of styrene. From the spectra of NbS catalysts after styrene oxidation, the strong, sharp and well defined absorption bands in the 1600–1700 cm^{-1} region, characteristic of carbonyl groups produced from oxidation of styrene are detected. This indicates clearly the

presence of product with aldehyde group. However, a large band was observed on catalysts after oxidation of benzene and toluene in the same zone. This large band can be assigned to the water molecules adsorbed in our catalysts. This is in accordance with extreme low conversion of benzene and toluene observed with all the catalysts. Complete desorption of all organic species adsorbed after 623 K, evidenced by IR spectra was confirmed by thermal analysis (not shown here). The presence of two bands at 1458 and 1494 cm^{-1} indicates the existence of strong acid sites [14]. These bands are significant for the catalysts used in oxidation of styrene. All the IR spectra will further be analyzed.

4. Conclusions

Niobium and niobium-cobalt-containing mesoporous redox molecular sieves analogue to MCM-41 were prepared by two different methods with the hydrothermal treatment. X-ray diffraction and TEM confirm the ordered mesoporous structure of all the Nb-MCM-41 and NbCo-MCM-41 samples prepared (except NbCoS sample prepared with sodium silicate) with TEOS and sodium silicate as silica source. This ordered structure can be affected by synthesis method due to the instability of the niobium precursor and metal composition. The incorporation of metal ions is favored with sodium silicate as silica

source while a less well ordered structure is obtained. The synthesis method can influence the activity of the Nb-MCM-41 catalyst and rate of the oxidation reaction.

All the materials synthesized show a high activity in oxidation of styrene and a low or very low activity in oxidation of benzene and toluene, respectively, with H_2O_2 . It is very surprising that the amorphous catalyst with NbCo gives the highest activity.

Acknowledgements

This work was performed within the framework of PAI-IUAP 5/1. V.P. thanks the Federal Scientific, Technological and Cultural Office of Premier Minister, Belgium (SSTC) for a scholarship (15 months) and the Direction Générale des Relations Extérieures (DGRE) du Gouvernement de la Région Wallonne, Belgique for a research grant (2×3 months). C.C. also thanks DGRE for research grants (2×3 months). The efficient assistance from Mrs. I. Su-Virlet is acknowledged.

References

- [1] K. Tanabe, S. Okazaki, *Appl. Catal. A* 133 (1995) 191–218.
- [2] P. Viparelli, P. Ciambelli, L. Lisi, G. Ruoppolo, G. Russo, J.C. Volta, *Appl. Catal. A: Gen.* 184 (1999) 291–301.
- [3] V. Pârvulescu, M. Ruwet, P. Grange, V.I. Pârvulescu, *J. Mol. Catal. A* 135 (1998) 75–88.
- [4] M. Ziolk, I. Nowak, *Zeolites* 18 (1997) 356–360.
- [5] Z. Ziolk, I. Sobczak, I. Nowak, P. Decyk, A. Lewandowska, J. Kujawa, *Microporous Mesoporous Mater.* 35–36 (2000) 195.
- [6] M. Ziolk, I. Sobczak, P. Decyk, I. Nowak, J. Kujawa, *Microporous Mesoporous Mater.* 35–36 (2000) 195–207.
- [7] J. Xin, J. Suo, X. Zhang, Z. Zhang, *New J. Chem.* 24 (2000) 569–571.
- [8] V.F. Stone Jr., R.J. Davis, *Chem. Mater.* 10 (1998) 1468–1474.
- [9] V. Pârvulescu, C. Dascalescu, B.L. Su, *Stud. Surf. Sci. Catal.* 135 (2001) 4772–4779.
- [10] V. Parvulescu, B.L. Su, *Catal. Today* 69 (2001) 315–322.
- [11] V. Parvulescu, C. Anastasescu, B.L. Su, *J. Mol. Catal. A* 198 (2003) 249–261.
- [12] V. Parvulescu, C. Anastasescu, C. Constantin, B.L. Su, *Catal. Today* 78 (2003) 477–485.
- [13] A. Tuel, *Microporous Mesoporous Mater.* 27 (1999) 151–167.
- [14] A. Jentys, K. Kleestorfer, H. Vinek, *Microporous Mesoporous Mater.* 27 (1999) 321–328.