

Bimetallic Ru-(Cr, Ni, or Cu) and La-(Co or Mn) incorporated MCM-41 molecular sieves as catalysts for oxidation of aromatic hydrocarbons

V. Pârvulescu^{a,b}, C. Anastasescu^a, B.L. Su^{b,*}

^a *Institute of Physical Chemistry "I.G. Murgulescu", Spl. Independentei 202, Bucharest, Romania*

^b *Laboratoire de Chimie des Matériaux Inorganiques, ISIS, The University of Namur (FUNDP), 61 rue de Bruxelles, B-50 Namur, Belgium*

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Abstract

Bimetallic Ru-(Co, Ni, Cu) and La-(Co or Mn) modified-MCM-41 molecular sieves are prepared by direct synthesis using surfactant templating process and evaluated in liquid phase selective oxidation of styrene and benzene with hydrogen peroxide. The fresh and used bimetallic molecular sieves were characterized by various techniques such as X-ray diffraction (XRD), N₂ adsorption–desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and infra-red (IR) spectroscopy. These materials have a typical MCM-41 structure. It is very interesting to note that bimetallic Ru or La-based MCM-41 catalysts have a very high conversion in hydroxylation of benzene to phenol, but a lower activity in oxidation of styrene to benzaldehyde, being contrary to the catalytic behavior of monometallic modified MCM-41 catalysts. It is shown that the activity and selectivity of bimetallic Ru, La-MCM-41 catalysts and the efficiency of H₂O₂ depend on the presence of the second metal, temperature and conditions of the reactions. The reaction mechanism is proposed on the basis of the observation of different reaction products.

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1. Introduction

MCM-41 molecular sieves, with high surface area, porosity and amorphous structure offer the possibility to directly incorporate the transition metal ions inside the mesoporous framework by substitution of Si atoms in regular tetrahedral positions. A large series of single metal ions such as Ti, V, Cr, Fe, Co, Ni, Mn, Cu, La and Ru have been used to modify the MCM-41 silica framework [1–5]. The obtained materials have shown the remarkable catalytic activity for partial oxidation of hydrocarbons under mild conditions. Some of these metal ions gave a high catalytic conversion but low selectivity; others led to the inverse results [6–10]. The incorporation of two different metals might therefore create new materials with different or new redox and acid properties. However, only a few studies concerned the synthesis and

catalysis of bimetallic ions modified mesoporous molecular sieves [11–16]. Some combinations of two metals such as Co–V, Co–Nb, Co–La, Ni–Ru, Ni–Cr, Ni–Ti, V–Ti, V–Cu and V–Co have been explored [17–19].

In the present work which is a continuation of our research, we report the incorporation of ruthenium in association with chromium, nickel or copper and lanthanum with cobalt or manganese in MCM-41 framework. The bimetallic silicate molecular sieves have been prepared by direct synthesis and their activity in oxidation of benzene and styrene with hydrogen peroxide in liquid phase has been evaluated. The oxidation products from these two reactions are phenol and benzaldehyde as antiseptic and artificial flavoring agents, respectively, and are widely used in commercial production. Moreover, the selective oxidation is a challenging subject for 21st century. By analyzing the reaction intermediates and products, we try to understand the reaction mechanism at molecular level in order to prepare the highly selective and efficient catalysts for oxidation of aromatics.

* Corresponding author. Tel.: +32-81-72-4531; fax: +32-81-72-5414.
E-mail address: bao-lian.su@fundp.ac.be (B.L. Su).

2. Experimental

2.1. Synthesis

RuCr-MCM-41, RuNi-MCM-41, RuCu-MCM-41, LaCo-MCM-41 and LaMn-MCM-41 were synthesized from sodium silicate, as the silica precursor, cethyltrimethylammonium bromide, as surfactant, and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ as metal sources. The gel obtained has the following molar composition: $\text{SiO}_2 : x\text{M}_1^{3+} : \text{M}_2^{n+} : 0.48 \text{ CTMAB} : 0.28 \text{ Na}_2\text{O} : 3.7 \text{ TMAOH} : 196 \text{ H}_2\text{O}$ (where $x = 0.04$, $\text{M}_1 = \text{Ru}$ or La ; $\text{M}_2 = \text{Cu}$, Ni , Cr , Co or Mn ; molar ratio $\text{M}_1/\text{M}_2 = 1$). For the successful incorporation of the metal ions into silica framework the precipitation of the metal hydroxides during gel preparation has to be avoided. The pH of the mixture was carefully adjusted to 10.5–11.0, by addition of H_2SO_4 solution. The gels obtained were treated into Teflon-lined steel autoclaves and heated to 5 days at 373 K. The solid product was recovered by filtration, washed with bi-distilled water and dried in air at 373 K. The metal contents were determined by elemental analysis and varied from 0.8 to 3.0 wt. %.

TG–DSC measurement of the synthesized samples with ruthenium shows a high thermal stability in air. Calcination of these samples was carried out at 723 K, 1 h in flow of N_2 , followed by 6 h in air. Calcination of the lanthanum modified samples was carried out at 823 K, 1 h in flow of N_2 , followed by 10 h in air.

2.2. Characterization

The fresh and used catalysts were characterized by XRD (Philips PW 170 diffractometer), N_2 adsorption–desorption (Micromeritics, Tristar), scanning electron microscopy (SEM) with a Philips XL-20 microscope and transmission electron microscopy (TEM) with Philips Tecnai microscope,

FTIR (Spectrum 2000, Perkin–Elmer) and TG–DSC analysis. Concentration of the metals into the MCM-41 was obtained by atomic absorption.

2.3. Catalytic properties in oxidation of styrene and benzene with H_2O_2 in liquid phase

The catalytic reactions were performed in the liquid phase with or without an organic solvent (acetonitrile). A mixture of 70 mg of the catalyst, styrene (2.7 g), acetonitrile, and hydrogen peroxide (30%) as oxidant, with a molar ratio: 1/3–6/3, or benzene (3.9 g) and hydrogen peroxide, with a molar ratio: 1/3, was continuously stirred in a glass flask with magnetic stirring for 12–48 h and a temperature range of 203–343 K. After reactions, the catalysts were separated by centrifugation and the oxidation products were analyzed using a GC equipped with a stainless steel columns and FID detector (Carlo Erba) with a column containing OV-101. The amount of the remaining unreacted H_2O_2 was quantified by conventional iodometry. The catalysts were reutilized in the oxidation reactions and characterized after each utilization. The leaching test was realized for all the catalysts.

3. Results and discussion

3.1. Catalysts characterization

XRD diffraction patterns of all the bimetallic silicates show at least two or three low-angle diffraction peaks, characteristic of mesoporous materials with hexagonal channel array and ordered pore system (Fig. 1).

Table 1 summarizes the surface areas (S_{BET}), pore sizes (ϕ_{BET}), lattice parameters (a_0) and framework wall thickness (w_t) obtained from N_2 adsorption–desorption and XRD techniques. The higher unit cell parameter a_0 compared with pure MCM-41 silica is an indication of the presence of metal ions in the molecular sieve framework. The low values of the

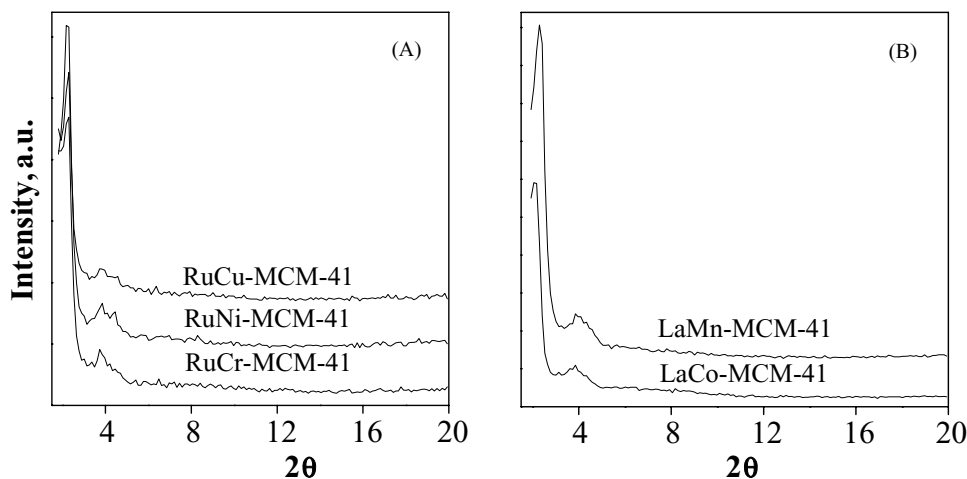


Fig. 1. X-ray powder diffraction patterns of the bimetallic molecular sieves.

Table 1
Physicochemical and catalytic properties of the bimetallic catalysts

| Sample | S_{BET} (m ² /g) | ϕ_{BET} (nm) | a_0 (nm) | w_t^a (nm) | Styrene | | Benzene | |
|-------------|--------------------------------------|--------------------------|------------|--------------|-----------------|--------------------------------|-----------|--------------------------------|
| | | | | | Conv. (%) | $C_{\text{eff.H}_2\text{O}_2}$ | Conv. (%) | $C_{\text{eff.H}_2\text{O}_2}$ |
| RuCu-MCM-41 | 640 | 2.70 | 4.4 | 1.70 | 7.5 | 10.1 | 75.1 | 25.5 |
| RuNi-MCM-41 | 805 | 2.75 | 4.5 | 1.75 | 8.1 | 1.2 | 18.6 | 6.3 |
| RuCr-MCM-41 | 705 | 2.65 | 4.5 | 1.85 | 50.8 | 18.6 | 60.3 | 21.7 |
| LaCo-MCM-41 | 740 | 2.70 | 4.6 | 1.90 | 1.8 | 1.2 | 0.6 | 0.8 |
| LaMn-MCM-41 | 789 | 2.65 | 4.3 | 1.65 | 7.4 | 24.1 | 65.9 | 24.8 |
| Ru-MCM-41 | 740 | 2.90 | 4.6 | 1.78 | 32.5 | 8.9 | 4.8 | 3.8 |
| La-MCM-41 | 755 | 2.55 | 4.2 | 1.64 | 19.7 | 7.4 | 4.8 | 10.6 |
| MCM-41 | 1123 | 2.65 | 4.3 | 1.68 | na ^b | na | na | na |

Reaction conditions: m_{cat} , 70 mg; reaction time and temperature, 2 h at 323 K.

^a Wall thickness $w_t = a_0 - \phi_{\text{BJH}}$.

^b na: no activity.

lattice parameters of the La containing mesoporous molecular sieves (Table 1), comparable with that of MCM-41 imply low incorporation of the metal. We can consider an influence of the second metal on the La cations and change in oxidation state of other. The violet color of LaMn-MCM-41 catalyst suggests the possibility of formation of Mn ions with a high oxidation state.

The pore size remains relatively constant while the surface area of our bimetallic modified samples, similar to the Ru or La-MCM-41 materials, is lower than that of monometallic Cr, Ni, Cu, Co or Mn-MCM-41 silicates [5,13]. The ratio of metal and oxygen ion radii ($R_{\text{M}(n+)}/R_{\text{O}(2-)} > 0.5$), an important structural parameter, shows for Ru and La incorporated MCM-41 molecular sieves a little possibility to be incorporated in the silica framework.

The highly ordered mesoporous framework with hexagonal array of cylindrical channels of the synthesized samples is confirmed by TEM images (Fig. 2). The SEM pictures of calcined samples, characteristic of metal ions modified MCM-41 materials [1,10] show the aggregates of submicron-sized globular particles (Fig. 3). The N₂ adsorption-desorption isotherms of all the calcined bimetallic silicates

(Fig. 4) are characteristic of mesoporous materials with uniform pore size. All the samples 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 pore size distributions determined by BJH method (Table 1) using the adsorption branch of isotherms are centered at a value of 2.7 ± 0.2 nm.

3.2. Catalytic properties in oxidation of aromatic hydrocarbons

The association of trivalent cations Ru or La with other transition metals modifies the activity and selectivity of the monometallic molecular sieves. The results and reaction conditions are summarized in Table 1. It can be seen that Ru-MCM-41 and La-MCM-41 give good conversion in oxidation of styrene but very low activity for benzene hydroxylation. While all the bimetallic catalysts, except RuNi-MCM-41 and LaCo-MCM-41, have a higher activity and efficiency of the H₂O₂ (H₂O₂ quantity used for oxidation/H₂O₂ quantity transformed) in the benzene hydroxylation. In the styrene oxidation, only RuCr-MCM-41

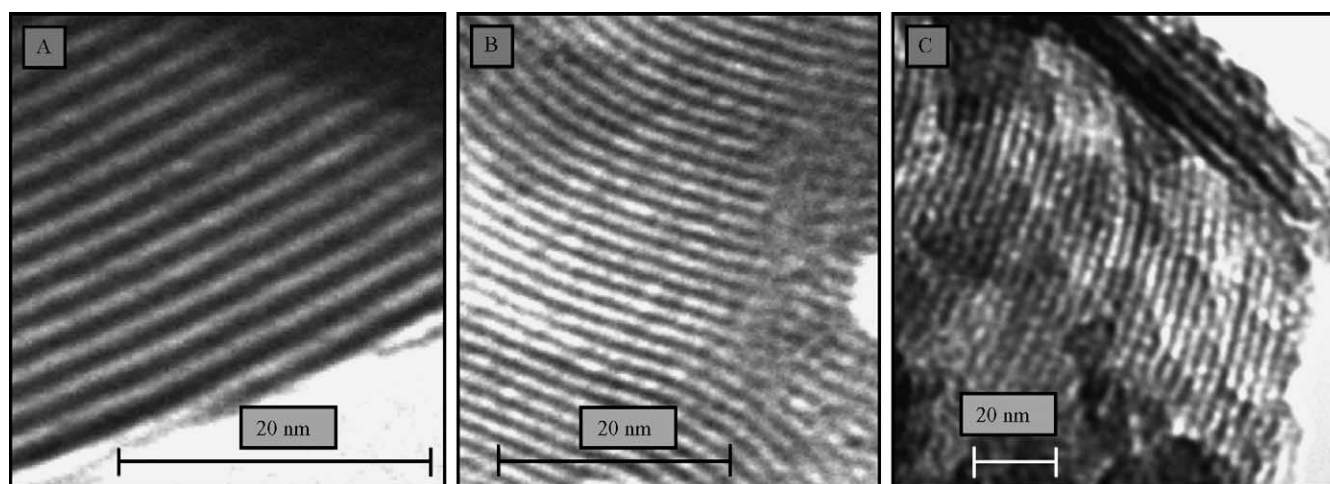


Fig. 2. TEM micrographs of the calcined RuNi-MCM-41 (A), RuCu-MCM-41 (B) and LaMn-MCM-41 (C) catalysts.

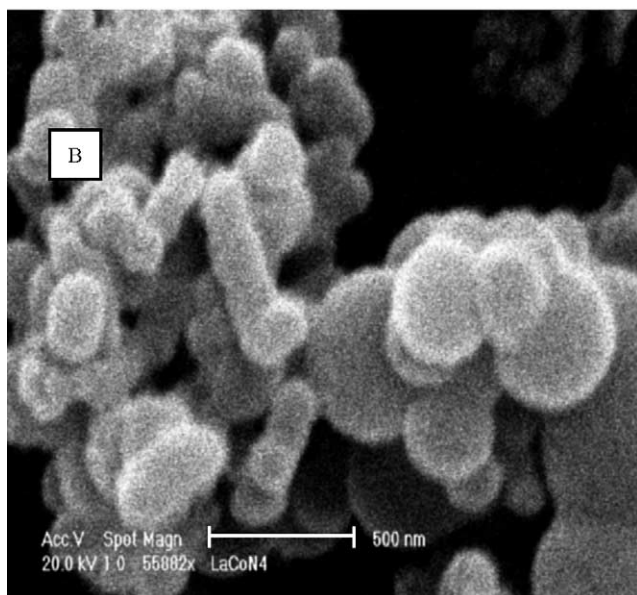
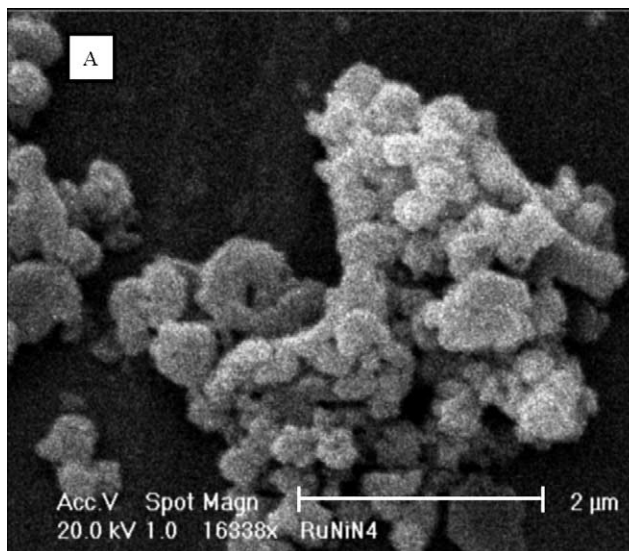


Fig. 3. SEM images of the calcined RuNi-MCM-41 (A) and LaCo-MCM-41 (B) molecular sieves.

gives a good conversion. In general, except LaCo-MCM-41, the conversion of catalysts in oxidation of benzene is higher than that in oxidation of styrene. This behavior is specific for these bimetallic samples since all the monometallic

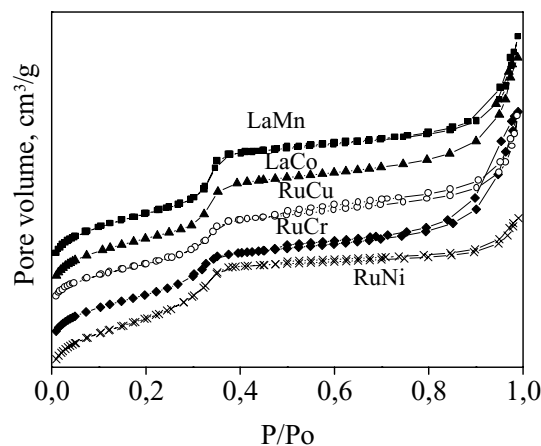
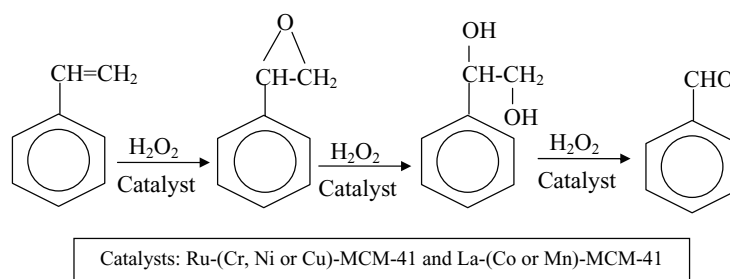


Fig. 4. N₂ adsorption–desorption isotherms of the bimetallic molecular sieves.

modified MCM-41 catalysts by incorporation of the same transition metals have a higher activity in oxidation of styrene and lower conversion in hydroxylation of benzene. LaCo-MCM-41 catalyst has a very low activity and RuCr-MCM-41 catalyst has a high activity both in the styrene and benzene oxidation. Under all investigated experimental conditions for oxidation of styrene, the principal reaction products detected by GC analysis are epoxy ethyl benzene (styrene oxide), phenyl ethanediol (styrene glycol) and benzaldehyde. It is obvious that the oxidation of styrene in the presence of H₂O₂ is a multi-step reaction. The styrene oxide is, very probably, firstly formed. The further reaction will give styrene glycol and finally to benzaldehyde as described in Scheme 1 of reaction mechanism which was well supported by our recent work using metal ions incorporated MCM-41 based membrane reactors for styrene oxidation. The styrene oxide was the only reaction product due to the very short residence time of reagent and product in membrane reactor compared with a batch reactor where the reagents and products were in continuous contact with catalysts. The presence of styrene oxide, styrene glycol and benzaldehyde in the discharged catalysts (see Section 3.3) proves our proposed reaction mechanism. The hydroxylation of benzene gives only the phenol.

Effects of the second metal incorporation, reaction time and temperature were evidenced. The activity of the catalysts



Scheme 1.

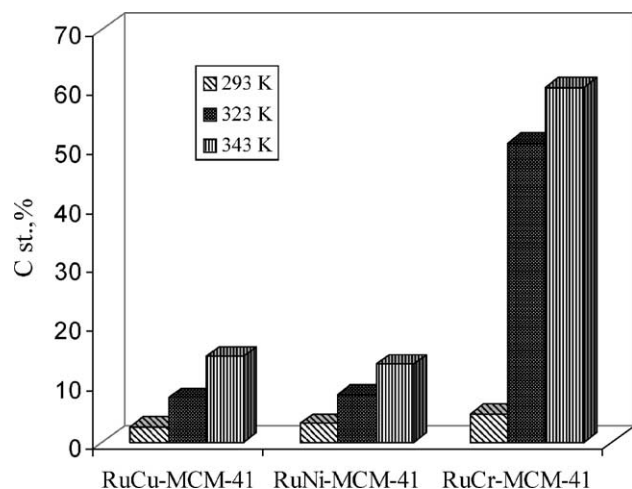


Fig. 5. Effect of temperature on the activity of the bimetallic Ru-MCM-41 catalysts in oxidation of styrene.

was found to increase with temperature (Fig. 5), time and decreasing the solvent molar percent.

3.3. Characterization of discharged catalysts and second or third cycle reaction

The IR absorbance spectra of adsorbed phase in discharged RuNi-MCM-41 catalyst after first cycle reaction upon desorption at a series of temperatures (293, 373, 623 and 723 K) are depicted in Fig. 6. The presence of different aromatic species such as styrene, benzaldehyde, styrene oxide and styrene glycol was noted (Table 2). 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. While after oxidation of benzene, only a weak adsorption of the aromatic species

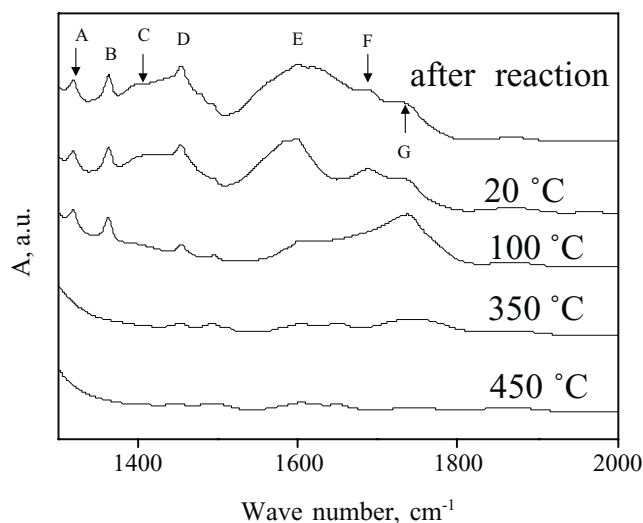


Fig. 6. FTIR spectra of the used RuNi-MCM-41 catalyst after desorption at different temperatures.

Table 2
Assignments of IR bands

| IR band | Wavenumber (cm ⁻¹) | Assignment ^a |
|---------|--------------------------------|---------------------------------------------------------|
| A | 1310 | OH in-plane bend (secondary OH of styrene glycol) |
| B | 1360 | OH in-plane bend (primary OH of styrene glycol) |
| C | 1392 | Typical aldehydic C–H bending vibration of benzaldehyde |
| D | 1465 | Aromatic ring modes |
| E | 1600 | Aromatic ring modes |
| F | 1700 | C=O stretch vibration of benzaldehyde |
| G | 1740 | Un-known |

^a On the basis of Refs. [20] and [21].

on the catalyst surface was evidenced. This could explain why our bimetallic modified catalysts are more active in hydroxylation of benzene than in oxidation of styrene.

Recycling of the catalysts in second or third-reaction cycles evidences an important increase in the conversion, but decrease in selectivity. Leached chromium and ruthenium species were detected after first reaction cycle. Higher $R_{M(n+)}/R_{O(2-)}$ ratio makes the large size ions such as Ru and La instable in the mesoporous silica framework. The increase in the catalytic activity and the decrease in selectivity in second and third reaction cycles could also be related to the presence of aromatic species (styrene, benzaldehyde and other products such as styrene oxide and styrene glycol) in the discharged catalyst evidenced by IR (Fig. 6). More adsorbed styrene, higher conversion. However, more adsorbed benzaldehyde, more undesired products and lower selectivity.

TEM images of the used catalysts show an ordered structure, indicating no effect of the reaction on the structure

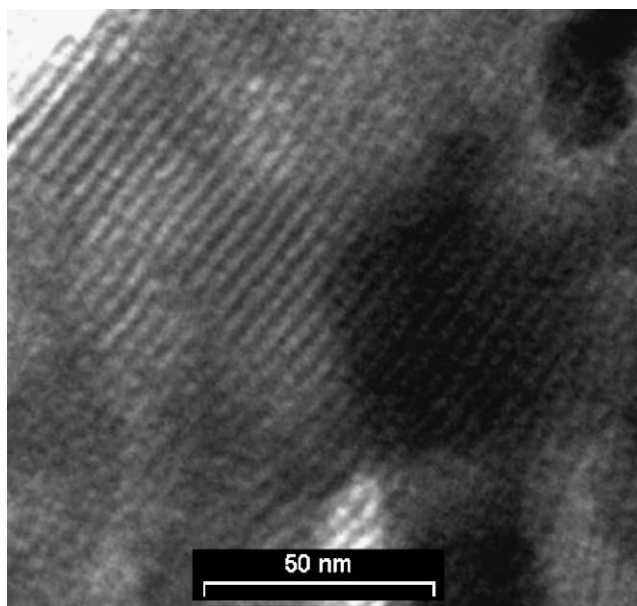


Fig. 7. TEM micrographs of the RuNi-MCM-41 samples after oxidation of benzene.

(Fig. 7). The SEM images of the used catalysts show that the morphology is the same with that of the as synthesized samples.

In conclusion, for the first time, the mesoporous bimetallic catalysts, with ruthenium or lanthanum, having the hexagonal array of the pore of MCM-41, have been synthesized. The bimetallic catalysts obtained are of high activity and selectivity in oxidation of styrene and benzene with hydrogen peroxide.

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