

# MCM-41 mesoporous molecular sieves supported nickel—physico-chemical properties and catalytic activity in hydrogenation of benzene

A. Lewandowska<sup>a</sup>, S. Monteverdi<sup>b</sup>, M. Bettahar<sup>b,\*</sup>, M. Ziolk<sup>a,\*</sup>

<sup>a</sup> Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznan, Poland

<sup>b</sup> Laboratoire de Catalyse Hétérogène, Faculté des Sciences, Université Henri Poincaré, BP 239, 54506 Vandoeuvre Cédex, France

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## Abstract

Siliceous, aluminosilicate and niobosilicate mesoporous molecular sieves of MCM-41 type have been used as matrices for nickel incorporated via the wet impregnation. The N<sub>2</sub> adsorption, XRD, H<sub>2</sub>-TPR and Ni dispersion study were applied for the characterization of the prepared catalysts. The metal–support interaction (MSI) was the highest in Ni/NbMCM-41 material as indicated from H<sub>2</sub>-TPR results, in which the highest dispersion of nickel occurs. Hydrogen chemisorption strength and the reducibility of Ni-species are inversely proportional to MSI strength. Both parameters determine the catalytic activity of the mesoporous materials in the hydrogenation of benzene at higher temperatures (423–473 K), whereas their activity at lower temperatures increases with increasing Ni dispersion. The kinetic study allows the determination of the activation energy in the benzene hydrogenation on Ni/MCM-41 which is very low, 36.5 kJ mol<sup>-1</sup>.

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## 1. Introduction

The high activity of nickel-containing catalysts in the desulfurization processes [1] as well as in the hydrogenation of aromatics, for example [2–6] are well established. Many parameters determining the catalytic activity in the hydrogenation processes have been already considered. Among them the role of a support nature was taken into account. Burch and Flambard [7] discussed Ni–support interaction with

silica, silica–alumina and titania as the supports. They considered the electronic and structural effects of the metal–support interaction (MSI) and their influence on the hydrogenolysis and hydrogenation of benzene. They concluded that it is not possible to differentiate between electronic and structural interactions stressing that these two parameters are, to some extent, mutually interdependent. However, there is an agreement in the literature [4,8] that at a low reaction temperature (323 K) benzene hydrogenation can be considered as a structure sensitive reaction and the rate of this reaction can be related to the unit area of metal. For poorly dispersed nickel/silica samples obtained by reduction at high temperature, the decrease in the intrinsic activity has been attributed to a strong metal–support interaction (SMSI) [4]. In the case of highly dispersed

\* Corresponding authors. Tel.: +48-61-8291243; fax: +48-61-8658008.

E-mail addresses: ziolk@amu.edu.pl, bettahar@lcah.uhp-nancy.fr (M. Bettahar).

<sup>1</sup> Tel.: +33-3-83912780; fax: +33-3-83912181.

materials, the changes in the catalytic activity were related to the combined effects of particle size, surface coverage with adsorbed species, and active site dimension [9]. Later [10], it was shown that the active sites are not related to certain special atoms but they depend on a statistical coverage of the surface by adsorbates.

The reducibility of nickel determining, to some extent, the activity of the catalyst strongly depends on the kind of elements incorporated into the support. It was concluded [11] that the specific activity of reduced nickel for benzene hydrogenation decreases with the increasing acid activity of the support in the order  $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{silica-alumina} > \text{Y zeolites}$ , but these activities remain constant in the faujasite acidity range from NaY to MgY zeolites.

All the mentioned features influencing the activity of nickel-containing catalysts are affected by nature of the support determining the MSI. Therefore, in the last decade many authors have studied various supports for nickel and tested the obtained materials in the hydrogenation of benzene. The growing interest in producing high-quality fuels caused the increase in the importance of hydrotreating processes in modern refinery schemes. Daza et al. [12] studying  $\text{Ni}_x\text{USY}$  zeolite catalysts have found that hydrogenation of benzene is proportional to the extent of nickel reduction, and hence to the number of reduced nickel atoms. Marecot et al. [8] considering structure sensitive or insensitive effect in the hydrogenation of benzene applied  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and MgO as supports for nickel. Ni/ $\alpha$ -alumina materials have been widely studied by Molina and Poncelet [13–15]. They stressed the role of nickel precursor in the preparation of highly active catalysts. The authors used Ni acetylacetonate for the wet impregnation of  $\alpha$ -alumina. Organometallic colloidal Ni precursor has been used in the impregnation of  $\gamma$ -alumina [5,6]. In this case the supported nanoparticles of metallic nickel were obtained and they were active in the gas phase hydrogenation of benzene.

The discovery of mesoporous molecular sieves of M41S family in 1992 [16] with the main representative of MCM-41, opened a new area in the application of these materials as supports for various metals and other catalytic active species. These mesoporous molecular sieves exhibit extremely high surface areas ( $>1000 \text{ m}^2 \text{ g}^{-1}$ ) and large, but well defined, pore sizes in the range of 2.0–30 nm, showing a relatively narrow pore size distribution. MCM-41 materials present

hexagonal arrangement of parallel mesopores and originally they were synthesized in the siliceous form. Very soon, after the first synthesis, many laboratories incorporated various elements together with siliceous into the framework of MCM-41 molecular sieves, for instant aluminum, vanadium, niobium, etc., changing the physico-chemical properties of the material. Mesoporous molecular sieves of MCM-41 type have been already used as supports for nickel [17–20] and the obtained materials were applied in various processes: desulfurization of thiols and organic sulfides [17,18], deodorization [19] or hydrodechlorination [20]. According to our knowledge, these kinds of catalysts have not been used yet in the hydrogenation of aromatics.

The aim of our study was the preparation of nickel-containing mesoporous molecular sieves by the wet impregnation of siliceous, aluminosilicate and niobosilicate MCM-41 materials, their characterization and testing in the hydrogenation of benzene. The application of matrices containing various elements allows the study of the effect of MSI.

## 2. Experimental

### 2.1. Catalysts

Aluminosilicate, niobosilicate and pure siliceous mesoporous molecular sieves of MCM-41 type were synthesized according to the procedure described in [21] (for siliceous and aluminosilicate sieves) and in [22] for niobosilicate one. Siliceous MCM-41 was synthesized as follows. Fifty grams of distilled water was combined with 0.3 g of sulfuric acid (95%) with stirring, and 8.08 g of sodium silicate (27%  $\text{SiO}_2$  in 14% NaOH) was added under stirring. Then 83.75 g of a template/water mixture (cetyltrimethylammonium chloride, 25 wt.% solution in water) was added after 10 min. The formed gel was stirred for about 0.5 h. The pH was adjusted to 11 by dropwise addition of sulfuric acid with vigorous stirring, after that it was added 20 g of distilled water. The gel was loaded into a stoppered PP bottle and it was heated without stirring at 373 K for 24 h. The mixture was cooled to room temperature (RT), and the pH was adjusted to 11 by dropwise addition of sulfuric acid with vigorous stirring. This reaction mixture was heated again to

373 K for 24 h. The product was filtered and washed with distilled water, and it was dried in air at 333 K. In the same way aluminosilicate material was obtained.

The procedure of the NbMCM-41 preparation was slightly modified to compare with that of MCM-41 one. A quantity of 8.08 g of sodium silicate (27% SiO<sub>2</sub> in 14% NaOH) was added to 50 g of distilled water under stirring. A quantity of 83.75 g of a template/water mixture (cetyltrimethylammonium chloride, 25 wt.% solution in water) was added after 10 min. Then 6037 g of niobium oxalate solution (0.604 g of niobium oxalate in 5.433 g of 0.1 M oxalic acid) was slowly added to achieve Si/Nb ratio of 32. The formed gel was stirred and the following procedure was the same as that described above for siliceous MCM-41. The only difference was using oxalic acid for pH adjustment in the preparation of NbMCM-41.

The templates in the catalysts MCM-41 and NbMCM-41 were removed by calcination at 773 K for 2 h in helium flow and 18 h in air. Nickel nitrate solution was used for the impregnation of mesoporous matrices. The evaporated catalyst was wetted at RT with Ni(NO<sub>3</sub>)<sub>2</sub> solution, mixed for 15 min and treated in vacuum evaporator at 353 K. The amount of Ni(NO<sub>3</sub>)<sub>2</sub> was calculated for 3 wt.% loading of nickel. The impregnated materials were dried at 393 K for 1 h.

The calcination of the catalysts was carried out in a flow of air (flow rate = 150 cm<sup>3</sup> min<sup>-1</sup>). The catalyst was filled in a quartz reactor and it was heated from 298 to 773 K. A rate of heating was 5 K min<sup>-1</sup>. The sample was treated in a flow of air at 773 K for 4 h and cooled to RT.

## 2.2. Characterization of physico-chemical properties

### 2.2.1. Nitrogen adsorption/desorption

The textural properties of calcined materials were studied by means of N<sub>2</sub> adsorption/desorption (at 77 K with Micromeritics 2010 apparatus).

### 2.2.2. XRD studies

XRD patterns were recorded by TUR 42 diffractometer with Cu K $\alpha$  radiation.

### 2.2.3. H<sub>2</sub>-TPR

The temperature-programmed reduction (TPR) of the samples was carried out using H<sub>2</sub>/Ar (10 vol.%)

as reductant (flow rate = 32 cm<sup>3</sup> min<sup>-1</sup>). A 0.025 g of the sample was filled in a quartz tube, treated in a flow of helium at 673 K for 1 h and cooled to RT. It was then heated at a rate of 10 K<sup>-1</sup> to 1300 K under the reductant mixture. Hydrogen consumption was measured by a thermal conductivity detector in a Pulse-ChemiSorb 2705 (Micromeritics) apparatus.

### 2.2.4. Reduction of nickel

The reduction of the catalyst was performed in a flow of hydrogen (flow rate = 50 cm<sup>3</sup> min<sup>-1</sup>). The catalyst was placed in a quartz reactor and it was heated at a rate of 1 K min<sup>-1</sup> to 523, or 623, or 723 K. After the reduction, carried out overnight, the sample was cooled to the desirable temperature.

### 2.2.5. Hydrogen adsorption

The hydrogen adsorption on the reduced catalyst was carried out using a mixture of H<sub>2</sub>/Ar (100 ppm H<sub>2</sub>). A 0.13 g of the catalyst was reduced according to the procedure described above. After the reduction, the sample was treated in a flow of argon at the reduction temperature for 1 h (flow rate = 100 cm<sup>3</sup> min<sup>-1</sup>). It was then cooled to RT in a flow of argon. The hydrogen adsorption was carried out at RT in a flow of H<sub>2</sub>/Ar (flow rate = 50 cm<sup>3</sup> min<sup>-1</sup>).

The temperature-programmed desorption of hydrogen was performed using an argon flow after the hydrogen adsorption. The catalyst and a flow way were purged with argon at RT for 20 min. The system was then heated at a rate of 5 K min<sup>-1</sup> to the reduction temperature under the argon flow (50 cm<sup>3</sup> min<sup>-1</sup>). The amount of chemisorbed hydrogen was detected each 1.10 min with a thermal conductivity detector in Agilent G2890A series Micro GCs gas chromatograph, operated at 333 K.

## 2.3. Catalytic activity

### 2.3.1. Hydrogenation of benzene

The benzene hydrogenation was performed in a quartz reactor equipped with a thermocouple. A 0.05 g of a catalyst was placed in the reactor and it was reduced in a flow of hydrogen according to the procedure described in Section 2.2. The catalytic test was carried out using C<sub>6</sub>H<sub>6</sub>/H<sub>2</sub> (1 vol.% of benzene) as a reactant mixture (flow rate = 50 cm<sup>3</sup> min<sup>-1</sup>). It was carried out at various temperatures on the same catalyst.

The sample was heated or cooled at a rate of  $10 \text{ K min}^{-1}$ . Benzene and the reaction products were analyzed each 30 min with 5730A Hewlett Packard gas chromatograph, operated at a programmed temperature (from 353 K heated at a rate of  $4 \text{ K min}^{-1}$  to 413 K for 2 min) and with a flame ionization detector (FID).

### 2.3.2. Kinetic study

The kinetic study was performed in a quartz reactor equipped with thermocouple. A 0.01 g of the catalyst was placed in the reactor and it was reduced in a flow of hydrogen according to the procedure described in Section 2.2. The kinetic study were carried out using  $\text{C}_6\text{H}_6/\text{H}_2 + \text{He}$  as a reactant mixture (flow rate =  $100 \text{ cm}^3 \text{ min}^{-1}$ ). The partial pressure of hydrogen was changed. The tests were conducted at 373 K. The catalyst was cleaned in a hydrogen flow (flow rate =  $50 \text{ cm}^3 \text{ min}^{-1}$ ) after each test. The sample was heated from 373 to 573 K. A rate of heating was  $10 \text{ K min}^{-1}$ . The catalyst was treated in a flow of hydrogen at 573 K for 30 min and cooled to the desired temperature. The reaction products were analyzed by GC in the same conditions as for the hydrogenation of benzene.

## 3. Results

### 3.1. Physico-chemical properties

#### 3.1.1. Texture

The low temperature nitrogen adsorption isotherms enable calculation of the specific surface area, pore volume, pore diameter and pore size distribution. The results are given in Table 1. The  $\text{N}_2$  adsorption/desorption isotherms of MCM-41,

AIMCM-41-32 and NbMCM-41-32 samples are typical of mesoporous materials (type IV).

The above mentioned parameters partially depend on the nature of the matrix. The modification of mesoporous sieves accomplished by Ni impregnation causes the decrease of both the surface area and the pore volume. The NbMCM-41-32 nickel modified sample shows the most significant difference in the surface area and the pore volume in comparison with those of pure material. The average pore diameter does not change after Ni-impregnation of AIMCM-41-32 material, slightly decreases after Ni modification of siliceous MCM-41, and significantly decreases when NbMCM-41-32 matrix is used as Ni support. The latter feature can be due to the growth of wall thickness increasing by the chemical interaction between Ni and Nb species after Ni modification of NbMCM-41.

X-ray diffraction patterns of mesoporous molecular sieves of MCM-41 type exhibits four peaks in the low angle range. The presence of these peaks in the XRD pattern is due to the hexagonal arrangement of mesopores. The modification of mesoporous materials by Ni-impregnation does not change the hexagonal ordering of the materials as shown in Fig. 1.

Both XRD and  $\text{N}_2$  sorption studies indicate that the mesoporous MCM-41 type structure is preserved after nickel impregnation.

#### 3.1.2. Surface properties

All the Ni modified samples studied in this work became gray or light gray after calcination due to the oxidation of Ni. The wet impregnation with the nickel salt followed by the calcination results in the generation of Ni-oxide species. This kind of Ni-species either can undergo the auto-reduction during the activation at the inert atmosphere (e.g. helium flow) or can remain

Table 1  
Characterization of the catalysts

Catalyst <sup>a</sup>	Preparation	Surface area ( $\text{m}^2 \text{ g}^{-1}$ ) (BET)	Pore volume ( $\text{cm}^3 \text{ g}^{-1}$ ) (BJH-ads)	Average diameter of pores (nm) (BJH-ads)	Wall thickness (nm)
MCM-41	Synthesis	1040	1.50	4.9	0.38
Ni/MCM-41-3	Impregnation	970	1.29	4.8	0.44
NbMCM-41-32	Synthesis	1031	1.17	4.1	0.50
Ni/NbMCM-41-32-3	Impregnation	814	0.79	3.7	0.73
AIMCM-41-32	Synthesis	986	1.14	4.3	0.53
Ni/AIMCM-41-32-3	Impregnation	915	1.08	4.3	0.56

<sup>a</sup> Number 32 indicates Si/Nb ratio. The last number in the impregnated samples denotes Ni weight percentage.

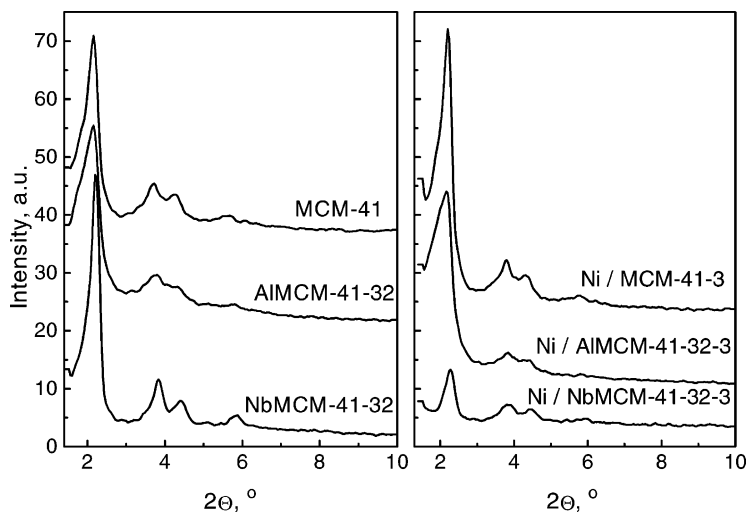


Fig. 1. XRD patterns.

in the parent form. The possible auto-reduction has to depend on the nature of a support. The H<sub>2</sub>-TPR profiles shown in Fig. 2 allow us to estimate Ni-species formed after 1 h activation of the calcined samples in helium flow at 673 K. The role of a kind of matrix is well evidenced from these profiles. Siliceous MCM-41 supported nickel indicates four components in a broad peak with the final maximum at 715 K. They can be

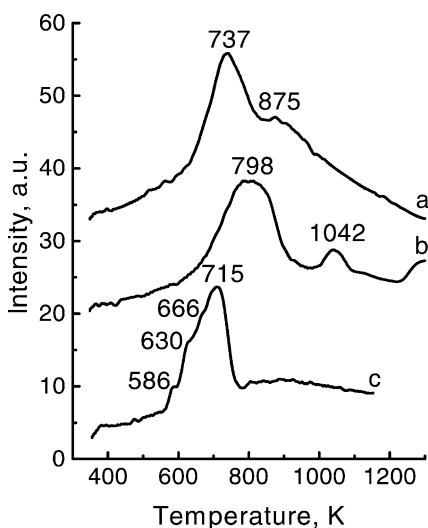


Fig. 2. H<sub>2</sub>-TPR profiles of nickel-containing catalysts: (a) Ni/AIMCM-41-32-3; (b) Ni/NbMCM-41-32-3; (c) Ni/MCM-41-3.

either due to the reduction of various nickel species or to the gradual reduction of one nickel oxide species, the first being more probable. The black color of the reduced material suggests the reduction of Ni-species to Ni<sup>0</sup>.

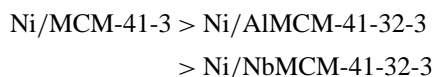
In the case of nickel loaded on AIMCM-41 and NbMCM-41 materials, the H<sub>2</sub>-TPR profiles differ from that of Ni/MCM-41 one. The Ni/AIMCM-41-32-3 TPR profile is very similar to that registered earlier [17,19]. The peak at 737 K is due to the reduction of Ni-oxide (most probably NiO) species to metallic nickel, whereas the second peak originates from the reduction of cationic form of nickel. The latter indicates that during the impregnation a partial cation exchange occurred and a part of nickel is located in the extra framework cation positions of AIMCM-41 molecular sieve. It is probable that due to the great free space in the pores of MCM-41 sieves (~70 vol.%), the wetted material treated with the solution in the impregnation procedure in fact possesses solution in the pores. That leads to the partial cation exchange. In the H<sub>2</sub>-TPR profile of Ni/NbMCM-41-32-3 the peaks above 1000 K are due to the reduction of niobium located in the framework [23]. A broad peak at a lower temperature most probably covers the maxima of the reduction of various Ni-oxide species.

It is worthy of notice that the reducibility of Ni-oxide species depends strongly on the nature of

Table 2  
The effect of the reduction temperature on Ni dispersion

Catalyst	Reduction temperature (K)	Dispersion, $N_S/N_T$	Metallic area ( $\text{m}^2 \text{g}^{-1}$ )
Ni/AlMCM-41-32-3	723	0.12	3.56
Ni/AlMCM-41-32-3	623	0.10	3.15
Ni/AlMCM-41-32-3	523	0.02	0.57

the mesoporous matrix. The maximum temperature of the hydrogen reduction of these species is an important parameter allowing us to propose the following order of the catalyst reducibility:



The reducibility of Ni-species depends on nickel–support interaction which seems to be the highest when Nb-containing matrix is used. The SMSI causes the more difficult reduction of nickel species with hydrogen.

As the reducibility of nickel species depends on the nature of the matrix one can expect that a kind of matrix will affect the dispersion of metal. The dispersion of nickel and the metallic area were first studied in the dependence on the reduction temperature. Table 2 exhibits the results obtained for Ni/AlMCM-41-32-3 material. Both parameters, dispersion and metallic area, increase with increasing reduction temperature. However, the increase of the reduction temperature from 623 to 723 K only slightly increases both parameters. Therefore, for the investigation of the role of matrix in the dispersion of nickel, the reduction was carried out at 623 K. The results are summarized in Table 3. The lowest dispersion and metallic area, occur when siliceous MCM-41 is used as Ni–support. Both, dispersion and metallic area, are comparable for two other matrices, and are the highest in the case of Ni/NbMCM-41.

Table 3  
The influence of mesoporous matrix on Ni dispersion

Catalyst	Reduction temperature (K)	Dispersion, $N_S/N_T$	Metallic area ( $\text{m}^2 \text{g}^{-1}$ )
Ni/MCM-41-3	623	0.07	2.27
Ni/AlMCM-41-32-3	623	0.10	3.15
Ni/NbMCM-41-32-3	623	0.11	3.40

The temperature-programmed desorption of chemisorbed hydrogen (TPD- $\text{H}_2$ ) allows differentiation between various types of Ni metal species. The effect of the reduction temperature on the desorption of hydrogen is illustrated in Fig. 3A. The amount of  $\text{H}_2$  desorbed is the highest when the reduction of Ni/AlMCM-41-32-3 is carried out at 623 K which is due to the maximum  $\text{H}_2$  chemisorption at this conditions. Therefore, this reduction temperature was applied for further study. The TPD- $\text{H}_2$  profiles presented in Fig. 3B are in good agreement with the results of  $\text{H}_2$ -TPR study discussed above. Ni/MCM-41 material exhibits minimum three shoulders in the TPD profile. Two kinds of metallic nickel can be concluded from two hydrogen desorption peaks from Ni/AlMCM-41. They can be assigned as follows: one to metal formed from the reduction of nickel cations located in the extra framework positions and the second to the desorption of hydrogen chemisorbed on nickel formed from Ni-oxide species. The hydrogen desorption from Ni/NbMCM-41-32-3 is characterized by one broad peak (like in  $\text{H}_2$ -TPR profile, Fig. 2)—one cannot exclude that it covers  $\text{H}_2$  desorption from various species.

### 3.2. Catalytic activity

#### 3.2.1. Hydrogenation of benzene

Ni/AlMCM-41-32-3 mesoporous catalyst has been chosen for testing the effect of the reduction temperature on the activity in the hydrogenation of benzene.

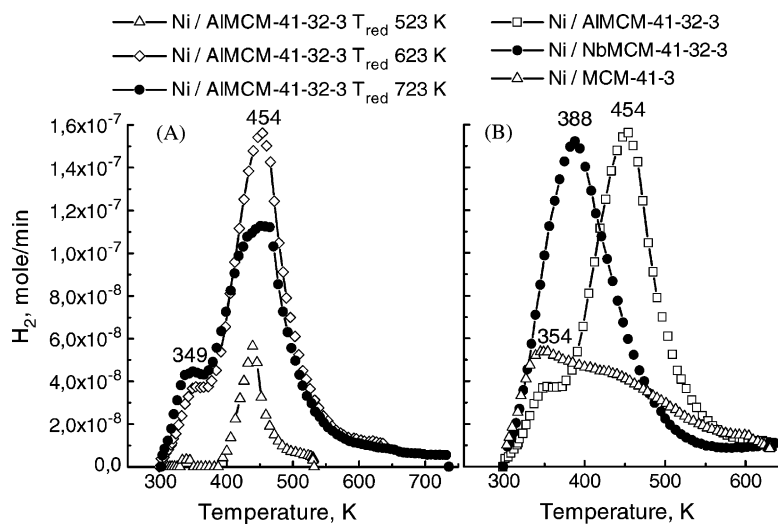


Fig. 3. TPD-H<sub>2</sub> profiles: (A) the dependence on the reduction temperature; (B) the dependence on the support (the reduction temperature was 623 K).

The results are shown in Fig. 4. There is almost no difference in the conversion of benzene on the catalyst reduced at 623 and 723 K in the temperature range of 325–473 K. The maximum conversion (98%) is achieved at 423–473 K. The material reduced at 523 K

exhibits the lower activity in almost entire range of temperatures.

The stability of the above mentioned catalyst was measured at 448 K (Fig. 5). The catalysts reduced at 723 and 623 K are highly stable for 14 h of the reaction

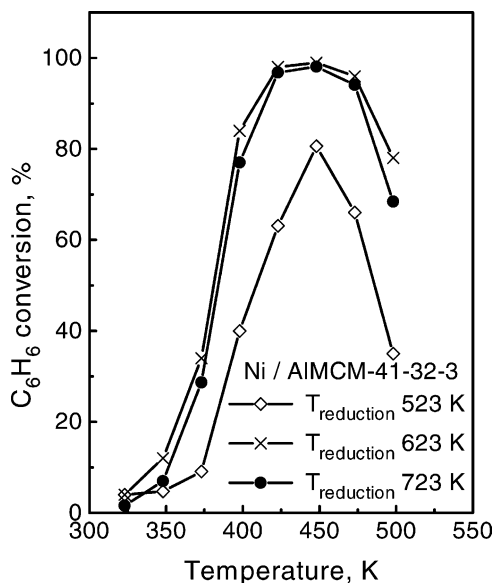


Fig. 4. The influence of the reduction temperature on the hydrogenation of benzene.

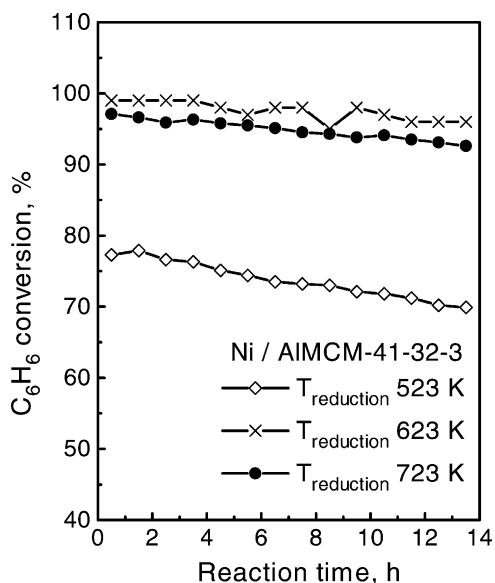


Fig. 5. The stability of Ni/AIMCM-41-32-3 reduced at various temperatures in the hydrogenation of benzene at 448 K.

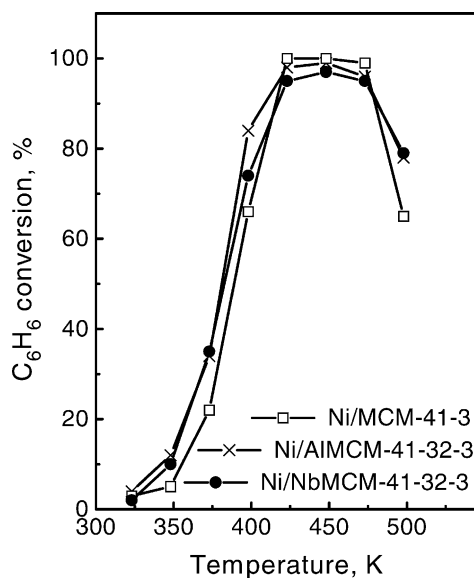


Fig. 6. The role of Ni-matrix in the hydrogenation of benzene on the catalysts reduced at 623 K.

showing a slight decrease of benzene conversion during this time. The catalyst reduction at 723 K gives rise to a little higher conversion of benzene than that noted after the reduction at 623 K. The material reduced at 523 K is not only less active but also its stability is lower—a higher decrease in the benzene conversion with the reaction time is observed.

The activity of the other Ni-impregnated mesoporous molecular sieves (Ni/MCM-41-3 and Ni/NbMCM-41-32-3) was tested after the reduction of the samples at 623 K. The results are plotted in Fig. 6. The sequence of the catalytic activity depends on the reaction temperature. At lower temperatures (358 and 373 K) the activities of Ni/AlMCM-41-32-3 and Ni/NbMCM-41-32-3 were almost the same and they were much higher than the activity of Ni/MCM-41-3 material. At the higher temperature range (423–473 K), in which the maximum activity of all catalysts is achieved, the sequence of the benzene conversion differs from that at low temperatures. It is referred to the initial activity because the catalysts are deactivated at various levels. Fig. 7 shows the reaction curves plotted for 14 h of the reaction performed at 448 K. Ni/AlMCM-41-32-3 catalyst exhibits the highest activity and stability, whereas the deactivation of Ni/MCM-41-3 sample is very fast. It is noteworthy

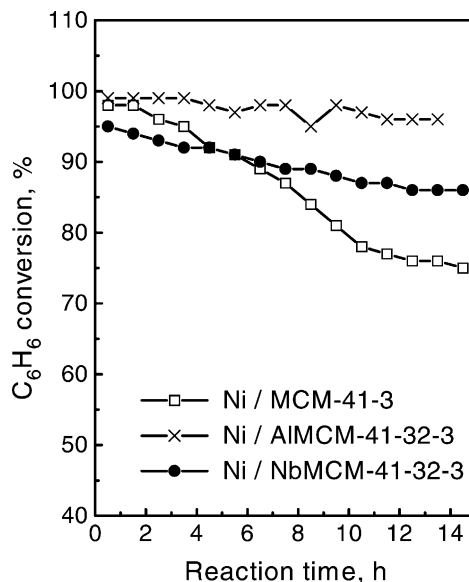


Fig. 7. The stability of the catalysts reduced at 623 K in the benzene hydrogenation at 448 K.

that the dispersion of nickel as well as Ni-support interaction on siliceous MCM-41 support are the lowest among all matrices applied. It can be postulated that the migration of nickel clusters during the reaction is easier on MCM-41 than on the other supports. The migration leads to the coalescence of Ni clusters and the decrease of Ni dispersion. This behavior can be considered as the reason of the deactivation of Ni/MCM-41-3 catalyst. However, the differences between low and high temperature results are very low and the above discussion could be treated rather as a hypothesis which requires another proofs in future.

In all the catalytic tests applied the only product of the benzene hydrogenation was cyclohexane.

### 3.2.2. Kinetic study

Kinetic study was carried out using Ni/MCM-41-3 catalyst showing the lowest activity at a low temperature range. This material exhibits about 2% of benzene conversion in the reaction conditions used. The only product was cyclohexane.

Fig. 8 shows the dependence of the reaction rate on a partial pressure of hydrogen and a partial pressure of benzene. The partial reaction orders with respect



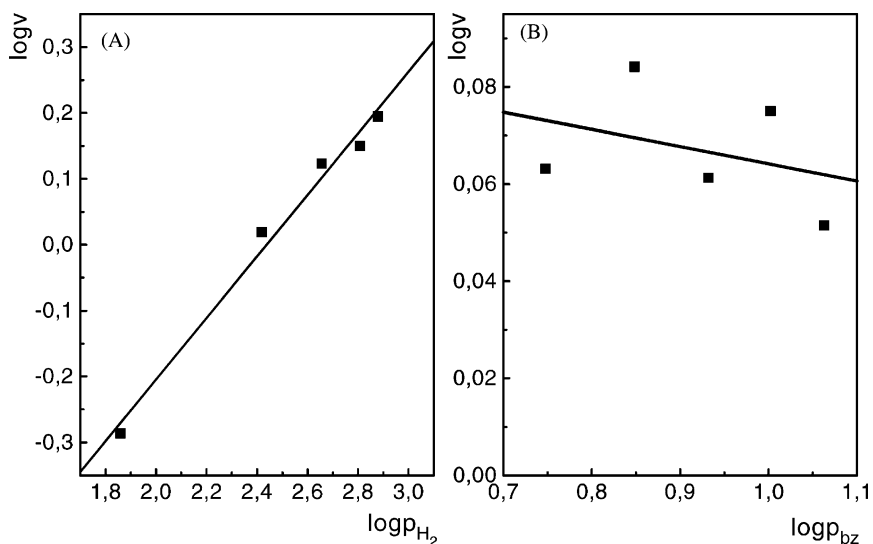


Fig. 8. Dependence of the reaction rate on a partial pressure of hydrogen and benzene: (A) related to H<sub>2</sub> pressure; (B) related to benzene pressure.

to hydrogen and benzene partial pressures are  $n_H = 0.46$  and  $n_B = 0$ , respectively, for the reaction rate equation

$$v = kp^{n_H} p^{n_B}$$

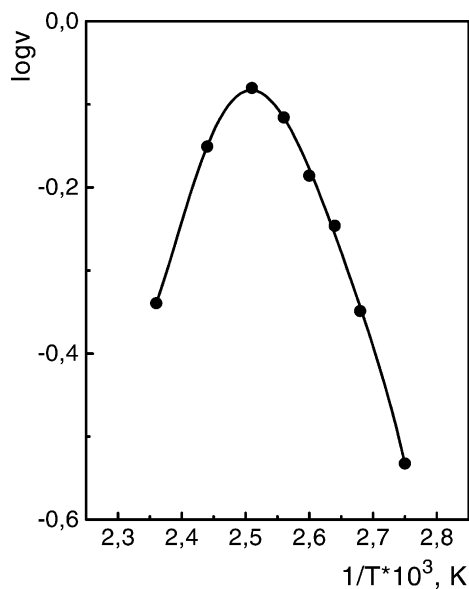


Fig. 9. The Arrhenius plot: hydrogen pressure, 72 Torr; benzene pressure, 3.73 Torr (1 Torr = 133.32 N m<sup>-2</sup>).

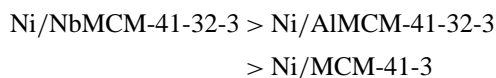
This results are in agreement with the literature data [2,10].

The Arrhenius plot (Fig. 9) shows the changes of the reaction rate with rising temperature. The reaction rate increases in temperature range 363–398 K. The curve maximum is located at 398 K. The reaction rate decreases above 398 K. The activation energy in the reaction of benzene hydrogenation calculated from the Arrhenius plot is 36.5 kJ mol<sup>-1</sup>.

#### 4. Discussion

Mesoporous molecular sieves of MCM-41 type are attractive supports for metals not only due to their very high surface areas but also due to easy modification of components building the framework of the sieves. The nature of elements incorporated into the skeleton of the materials determines the interaction between metal and a support. In this study three various mesoporous matrices were applied: pure siliceous (MCM-41), aluminosilicate (AlMCM-41-32), and niobosilicate (NbMCM-41-32). They were modified with 3 wt.% of Ni via the wet impregnation. Thanks to various elements which build the mesoporous framework one could achieve various nickel–support interaction. The following sequence of the strength of

the MSI:



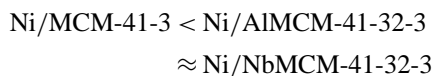
was established on the basis of the samples reduction with hydrogen ( $\text{H}_2$ -TPR profiles). The higher the MSI, the lower the reducibility of Ni-species.

It is worthy of notice that the level of nickel dispersion is well correlated with the determined strength of nickel–support interaction. The highest MSI was registered on Ni/NbMCM-41-32 and the same sample exhibits the highest dispersion of nickel and metallic area. It is probable that the strong interaction between nickel and niobium in the mesoporous molecular sieves framework prevents the small Ni clusters from coalescence and growth in size. Because of that the dispersion of nickel is high.

The MSI determines also the strength of hydrogen chemisorption estimated on the basis of TPD- $\text{H}_2$  experiments. The comparison of TPD- $\text{H}_2$  patterns presented in Fig. 3 allows the conclusion that the desorption of hydrogen chemisorbed on nickel is easier when Ni strongly interacts with the support, as in Ni/NbMCM-41-32-3 sample. The strong metal–niobium (support) interaction has been already found in Cu–NbMCM-41 materials [24] and Ni/Nb–Si oxides [25]. However, in the case of Cu–NbMCM-41, where copper species occupy the extra framework positions, the Cu–Nb interaction differs from that observed in the impregnated samples. The interaction of isolated copper cations occurs with  $\text{NbO}^-$  species and exhibits ionic character. Thanks to that the reducibility of copper species increases [24]. In the case of the catalyst prepared via impregnation, the Ni–Nb interaction exhibits the metallic character and the increase of its strength causes the decrease of nickel reducibility with hydrogen.

Both the reducibility of nickel and the strength of hydrogen chemisorption influence the catalytic activity and stability of the materials in the benzene hydrogenation. The consideration of the sequence in the benzene conversion on various catalysts (Fig. 6) depending on the temperature region clearly shows that in the low temperature range the activity changes according to the nickel dispersion, i.e. in the following

order:



This relationship confirms the structure sensitivity of the benzene hydrogenation at low temperatures postulated in the literature [4,8]. At higher temperatures, when the maximum activity is reached (423–473 K), the sequence in the catalytic activity seems to be opposite to that shown above, and can be correlated with the strength of hydrogen chemisorption. However, the differences are very small, maybe within experimental error. The stronger the  $\text{H}_2$  chemisorption, the higher the activity.

The greater difference has been noted in the deactivation of the catalysts based on various supports (Fig. 6). The lowest stability was found in the case of Ni/MCM-41. It can be postulated that this behavior is due to the growth of the metal crystalline size. One can expect that at the reaction temperature the migration of nickel particle occurs easier when Ni–support interaction is lower. That is a case of Ni supported on siliceous MCM-41. The above hypothesis requires further studies.

The kinetic study indicates that the activation energy in the benzene hydrogenation ( $36.5 \text{ kJ mol}^{-1}$ ) carried out on Ni/MCM-41-3 is much lower than that described in the literature [8] for nickel loaded on various supports ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , MgO).  $E_a$  calculated by Marecot et al. [8] for these matrices varies from 50.5 to  $52.3 \text{ kJ mol}^{-1}$  depending on both nature of a support and Ni loading.

A low activation energy calculated in this work confirms that mesoporous molecular sieves are very attractive supports for nickel active in the hydrogenation of benzene.

## 5. Conclusions

1. The incorporation of Al or Nb into the siliceous MCM-41 sieve framework increases the strength of Ni (metal)–support interaction (MSI), which is the highest for Ni/NbMCM-41 based on the highest reduction temperature of Ni.
2. MSI determines Ni dispersion—the higher the MSI the higher the dispersion of nickel.

3. H<sub>2</sub> chemisorption strength and the reducibility of Ni-species are inversely proportional to MSI strength.
4. At a low temperature the catalytic activity in the hydrogenation of benzene increases with Ni dispersion, whereas at higher temperatures (423–473 K), it is possibly determined by H<sub>2</sub> chemisorption strength and the reducibility of Ni-species.
5. The activation energy in the benzene hydrogenation is lower (36.5 kJ mol<sup>-1</sup>) on Ni/MCM-41 than that described in the literature [8] for Ni impregnated various oxides (50.5–52.3 kJ mol<sup>-1</sup>) making M41S materials attractive for use as support.

## References

- [1] M. Ziolk, M. Sugioka, Res. Chem. Intermed. 26 (2000) 385.
- [2] R.Z.C. van Meerten, J.W.E. Coenen, J. Catal. 37 (1975) 37.
- [3] R.Z.C. van Meerten, J.W.E. Coenen, J. Catal. 46 (1977) 13.
- [4] G.A. Martin, J.A. Dalmon, J. Catal. 75 (1982) 233.
- [5] D. Franquin, S. Monteverdi, S. Molina, M. Bettahar, Y. Fort, J. Mater. Sci. 34 (1999) 4481.
- [6] S. Lefondeur, S. Monteverdi, S. Molina, M. Bettahar, Y. Fort, J. Mater. Sci. 36 (2001) 2633.
- [7] R. Burch, A.R. Flambard, J. Catal. 85 (1984) 16.
- [8] P. Marecot, E. Paraiso, J.M. Dumas, J. Barbier, Appl. Catal. 74 (1991) 261.
- [9] G.A. Martin, J.A. Dalmon, C. Mirodatos, in: Proceedings of the Eighth International Congress on Catalysis, Vol. IV, Berlin, Verlag Chemie, Weinheim, 1984, p. 371.
- [10] C. Mirodatos, J.A. Dalmon, G.A. Martin, J. Catal. 105 (1987) 405.
- [11] J.T. Richardson, J. Catal. 21 (1971) 122.
- [12] L. Daza, B. Pawelec, J.A. Anderson, J.L.G. Fierro, Appl. Catal. A 87 (1992) 145.
- [13] R. Molina, G. Poncelet, J. Catal. 173 (1998) 257.
- [14] R. Molina, G. Poncelet, J. Phys. Chem. B 103 (1999) 11290.
- [15] R. Molina, G. Poncelet, J. Catal. 199 (2001) 162.
- [16] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
- [17] M. Ziolk, I. Nowak, I. Sobczak, A. Lewandowska, P. Decyk, J. Kujawa, Stud. Surf. Sci. Catal. 129 (2000) 813.
- [18] M. Ziolk, I. Nowak, I. Sobczak, H. Poltorak, Stud. Surf. Sci. Catal. 130 (2000) 3047.
- [19] M. Ziolk, I. Nowak, H. Poltorak, A. Lewandowska, I. Sobczak, Stud. Surf. Sci. Catal. 125 (1999) 691.
- [20] Y. Cesteros, P. Salagre, F. Medina, J.E. Sueiras, G.L. Haller, Stud. Surf. Sci. Catal. 135 (2001) 233.
- [21] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
- [22] M. Ziolk, I. Nowak, Zeolites 18 (1997) 356.
- [23] M. Ziolk, I. Sobczak, A. Lewandowska, I. Nowak, P. Decyk, M. Renn, B. Jankowska, Catal. Today 70 (2001) 169.
- [24] M. Ziolk, I. Sobczak, I. Nowak, P. Decyk, J. Stoch, Stud. Surf. Sci. Catal. 135 (2001) 151.
- [25] E.B. Pereira, M.M. Pereira, Y.L. Lam, C.A.C. Perez, M. Schmal, Appl. Catal. A 197 (2000) 99.