

Article

Ruthenium Catalysts Templated on Mesoporous MCM-41 Type Silica and Natural Clay Nanotubes for Hydrogenation of Benzene to Cyclohexane

Aleksandr Glotov ¹,*^D, Anna Vutolkina ^{1,2}^D, Aleksey Pimerzin ^{1,3}, Vladimir Nedolivko ¹, Gleb Zasypalov ¹^D, Valentine Stytsenko ¹, Eduard Karakhanov ² and Vladimir Vinokurov ¹

- ¹ Gubkin Russian State University of Oil and Gas, 65 Leninsky prosp., 119991 Moscow, Russia; annavutolkina@mail.ru (A.V.); aleksey@pimerzin.com (A.P.); nedolivko74@mail.ru (V.N.); gleb.zasypalov@mail.ru (G.Z.); vds41@mail.ru (V.S.); vinok_ac@mail.ru (V.V.)
- ² Lomonosov Moscow State University, 3, 1 Leninskie Gory, 119991 Moscow, Russia; kar@petrol.chem.msu.ru
- ³ Samara State Technical University, 244 Molodogvardeyskaya street, 443100 Samara, Russia
- * Correspondence: glotov.a@gubkin.ru

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Abstract: Mesoporous ruthenium catalysts (0.74–3.06 wt%) based on ordered Mobil Composition of Matter No. 41 (MCM-41) silica arrays on aluminosilicate halloysite nanotubes (HNTs), as well as HNT-based counterparts, were synthesized and tested in benzene hydrogenation. The structure of HNT core-shell silica composite-supported Ru catalysts were investigated by transmission electron microscopy (TEM), X-ray fluorescence (XRF) and temperature-programmed reduction (TPR-H₂). The textural characteristics were specified by low-temperature nitrogen adsorption/desorption. The catalytic evaluation of Ru nanoparticles supported on both the pristine HNTs and MCM-41/HNT composite in benzene hydrogenation was carried out in a Parr multiple reactor system with batch stirred reactors (autoclaves) at 80 °C, a hydrogen pressure of 3.0 MPa and a hydrogen/benzene molar ratio of 3.3. Due to its hierarchical structure and high specific surface area, the MCM-41/HNT composite provided the uniform distribution and stabilization of Ru nanoparticles (NPs) resulted in the higher specific activity and stability as compared with the HNT-based counterpart. The highest specific activity (5594 h⁻¹) along with deep benzene hydrogenation to cyclohexane was achieved for the Ru/MCM-41/HNT catalyst with a low metal content.

Keywords: ruthenium catalysts; benzene hydrogenation; MCM-41; halloysite nanotubes; mesoporous aluminosilicates; MCM-41/HNT composite

1. Introduction

In the modern global quest for cleaner fuel production, benzene has been identified as a gasoline component that should be reduced. According to the modern clean fuel standard regulations in the US, specifically Mobil Source Air Toxics II (MSAT II), refiners are required to reduce benzene in gasoline to 0.62 vol% on an average annual basis. In Europe and in many other regions, a regulation of 1.0 vol% maximum of benzene in gasoline has also been adopted to limit benzene [1–3]. The selective removal of benzene and other aromatics from motor fuels by hydrogenation ensures a control of the particulate emissions and cetane number boost of diesel [2].

There are two main strategies for benzene hydrogenation: partial hydrogenation aimed to cyclohexene production and deep hydrogenation to cyclohexane [4–7]. The former often requires bimetallic systems as catalysts, such as Ru–Zn, Ru–Co, Ru–Cu and Ru–lanthanides, promoted by various additives or non-promoted [4,7–9]. Another approach is to design hydrophobic/hydrophilic



supports and use water as a solvent to prevent cyclohexene excess by hydrogenation (water solubility of cyclohexene and benzene is higher than that of cyclohexane alone) [4,10].

In refineries, benzene hydrogenation to cyclohexane performs in the presence of Group VIII metal catalysts such as Ni, Pt, Pd and Ru at temperatures in the range 150 °C–220 °C under H₂ pressure up to 10 MPa [11–16]. For deep benzene hydrogenation at lower temperatures, Ni- or Pt-containing catalysts are usually employed as they are the most active [11,17–19]. These catalysts, however, have a low tolerance to various poisons in the feed that should be preliminary refined [18–20]. The conventional sulfide NiMoSx and NiWSx catalysts have a good activity only at severe conditions (T > 300 °C and pressures 5 MPa and higher), therefore, sophisticated equipment is needed, causing higher investment and process costs [19,21,22].

The needs for effective catalysts ensuring benzene removal under mild conditions have initiated a number of studies aimed at designing new catalytic systems comprising noble metals on supports such as alumina, zeolites and ordered mesoporous silica, e.g., SBA-15, Mobil Composition of Matter No. 41 (MCM-41) [11,17–19,23–25]. There are reports on the application of Ru/C, Ru/graphene and Ru/carbon nanotubes in deep benzene hydrogenation [9,26]. Some research used bimetallic systems with noble metals [23,27,28].

The most promising catalytic systems for benzene hydrogenation to cyclohexane are those comprising ruthenium, thanks to its high activity and low cost compared to other noble metals [25,29–31]. The prospects stated have been confirmed by the application of Ru/zeolite catalysts for benzene hydrogenation [25,32]. In the operation of zeolite-based catalysts, however, diffusion limitations arise due to very narrow channels inside this support. Thanks to the intrinsic well ordered structure, a high specific surface area (about 1000 m².g⁻¹) and adjusting pore sizes (2–4 nm), mesoporous silicates are considered as the promising supports for highly dispersed catalysts [33–36]. Among them, MCM-41 (Mobil Composition of Matter No. 41) is an advanced mesoporous material, with a hierarchical hexagonal 2D structure belonging to the silicate family, and is the most attractive [37–39]. The mean size of MCM-41-supported Ru particles is about 1.8 nm with a metal dispersion of 62% [40]. However, MCM-41 silica possesses a low thermal stability (700°C) and mechanical strength (about 220 MPa) that restricts its industrial application [34,41].

As the carriers for hydrogenation catalysts, natural clay nanotubes such as halloysite are of particular interest [16,42–45]. Halloysite is a natural clay aluminosilicate nanotube from the kaolinite group named after the Belgian geologist Omalius d'Halloy who was the first to describe the mineral. Halloysite nanotubes (HNTs) form by the rolling of the kaolin sheets into tubes (length of 0.5–2 μ m, inner diameter 10–30 nm, depending on deposit) with negative an outer surface (tetrahedral silanol groups) and an octahedral alumina-composed positive charged inner surface [42,46]. Halloysite has the appropriate specific surface area (50–100 m².g⁻¹), high ion-exchange capacity and mesoporous structure that enables the synthesis of highly active ruthenium catalysts and new materials applied for heterogeneous catalytic systems [15,47,48]. Thus, a new approach was developed, where HNTs act as a template for the self assembling of the mesoporous silica MCM-41 type on the outer surface of HNTs. As a result, high-porous meso silica arrays on HNTs with enhanced thermal and mechanical stabilities were formed [49].

The present work was devoted to the catalytic evaluation of ruthenium catalysts based on ordered MCM-41 type silica arrays on aluminosilicate HNTs in comparison with a HNT-based counterpart, depending on the Ru content as well as the localization of active metal particles in benzene hydrogenation.

2. Results and Discussion

The structure of the well ordered mesoporous MCM-41 type silica assembled on the outer surface of HNTs, retained after Ru loading, was clearly indicated by transmission electron microscopy (TEM) (Figure 1). The core-shell hexagonal 2D structure produced by the cetyltrimethylammonium bromide (CTAB)-templated silica on the nanotubes as well as its Ru deposition are shown in Figure 1.

The mesoporous silica phase with a one-direction channel system bonded to the outer surface of aluminosilicate HNTs was kept during the metal loading under microwave irradiation [49].



Figure 1. Transmission electron microscopy (TEM) micrographs (**a**–**c**,**g**–**i**) and the Ru-nanoparticle size distribution (**d**–**f**,**j**–**l**) in catalysts Ru/ halloysite nanotubes (HNT) and Ru/Mobil Composition of Matter No. 41 (MCM-41)/HNT.

The retention of the MCM-41/HNT structure after Ru impregnation was also proved by low-temperature nitrogen adsorption/desorption technique. As shown in Figure 2, Ru/MCM-41/HNT catalysts were characterized by isotherms of IV type with a capillary condensation step in the range of relative partial pressures P/P₀ of 0.4–0.6, corresponding to the presence of a mesoporous framework (Figure 2a) [49,50]. Meanwhile, the N₂ isotherms for the Ru/HNT catalysts are of III type with a hysteresis loop at a P/P₀ ratio of 0.5–1.0, indicating a capillary condensation in the meso/macropores of halloysite lumen (Figure 2b) [15,16,29,45]. The pore size distribution for both the mesoporous MCM-41/HNT composite-supported and the pristine HNT-based Ru catalysts had a narrow peak centered at 30–32 Å (Figure 2, Table 1).

	Textural Characteristics				Ru, w			
Sample	S _{BET} , m ² ⋅g ⁻¹	D _p , Å	V_p, cm^3 g^{-1}	From XRF	From TPR-H ₂	From XRF (Recycled) *	Ru Average Particle Size, nm **	
HNT	70	70	0.16	-	-	-	-	
Ru/HNT(1)	68	69	0.14	0.74	0.80	0.62/0.62/0.61	3.6 ± 0.1	
Ru/HNT(2)	61	68	0.13	1.65	1.68	1.29/1.28/1.27	4.1 ± 0.1	
Ru/HNT(3)	56	67	0.11	2.82	2.75	2.14/2.12/2.09	5.4 ± 0.1	
MCM-41/HNT	520	28	0.43	-	-	-	-	
Ru/MCM-41/HNT(1)	433	30	0.34	0.74	0.82	0.68/0.68/0.67	3.4 ± 0.1	
Ru/MCM-41/HNT(2)	411	31	0.33	1.59	1.50	1.49	3.7 ± 0.1 6.7 ± 0.1	
Ru/MCM-41/HNT(3)	373	33	0.31	3.06	2.96	2.83	3.4 ± 0.1 7.2 ± 0.2	

Table 1. Ru content (from X-ray fluorescence (XRF) and temperature-programmed reduction (TPR-H₂)) and the textural characteristics of MCM-41/HNT and HNT-supported catalysts.

* Measured by XRF after 1 recycle for Ru/MCM-41/HNT (2 and 3) and after each of 3 recycles for other catalysts, ** According to TEM data.

The relative intensity of the shoulder in the range of 20–30 Å (Figure 2b,d) increased with the metal loading, which indicated the partial agglomeration of the Ru nanoparticles inside the pores leading to a decrease in pore volume. It also corresponded with the Ru average particle size calculated based on the TEM data. Thus, for both the MCM-41/HNTs and the pristine HNT-templated catalysts, the pores with more than 40 Å in diameter corresponding to HNTs were also observed [15,30]. The higher metal content and the lower area was found under the part of the pore size distribution curve between 40–80 Å due to the Ru loading into the lumen that was also depicted in the TEM images.

When the metal content increased, the specific surface area of the catalysts decreased. Thanks to the well ordered MCM-41 hexagonal porous arrangement, the S_{BET} for the composite-supported Ru catalysts was significantly higher compared to the pristine HNT-based counterparts. The impregnation of supports with an aqueous solution of ruthenium salt under microwave irradiation provided highly dispersed catalysts having metal nanoparticles being uniformly distributed over the carrier surfaces and in the lumen [15,45] (Figure 1). The impregnation procedure applied gave rise to the forming ruthenium nanoparticles with diameters of 3.6–5.4 nm in the inner surface of the halloysite. This fact was unusual because the positive charge of the lumen normally prevents ruthenium cation intercalation (Figure 1) [29,42,46]. Increasing the metal content leads to then formation and aggregation of partially outside nanoparticles, in accordance with the data published [16,47,48,51]. The average particle size for the Ru/HNT(1) catalyst was about 3.6 ± 0.1 nm and the size distribution curves were approximated by Weibull distribution. For two other counterparts with 1.7 and 2.8wt% of Ru the particles with 4.1 ± 0.1 and 5.4 ± 0.1 nm in diameter were formed, respectively (Table 1, Figure 1). Thus, the higher the metal loading, the higher are the sizes of the particles observed. Moreover, the particle size distributions curves were broadened. The well ordered MCM-41 hexagonal porous arrangement provided uniform particle size distribution. The unimodal distribution with an asymmetric peak for catalysts with a lower Ru content proved the selective nanoparticle intercalation into the mesoporous structure $(3.4 \pm 0.1 \text{ nm})$, while for Ru/MCM-41/HNT(2) and Ru/MCM-41/HNT(3), bimodal distribution was realized with particle diameters of 3.4 and $6.7-7.2 \pm 0.1$ nm, respectively, and Ru was intercalated into lumen.

The TPR-H₂ profiles for the Ru/HNT samples and the quantification data are presented in Figure 3 and Table 1, respectively. The ruthenium content was calculated based on the hydrogen consumption caused by the complete reduction of RuO₂.



Figure 2. Nitrogen adsorption/desorption isotherms (**a**,**c**) and the pore size distribution (**b**,**d**) for the MCM-41/HNT and the HNT-supported Ru catalysts.



Figure 3. TPR-H₂ profiles for the Ru catalysts templated on HNTs and the MCM-41/HNT composite (**a**) Ru/HNT(1) and Ru/MCM-41/HNT(1), (**b**) Ru/HNT(2) and Ru/MCM-41/HNT(2), (**c**) Ru/HNT(3) and Ru/MCM-41/HNT(3).

The TPR profiles of the Ru/HNT catalyst had one intense peak at 140 °C corresponding to the reduction of RuO_{2} , which was strongly bonded to the outer surface of the nanotubes [15,30]. An increase in the metal content followed by a partial Ru intercalation into the HNTs lumen, broadens the peak and

shifts it to a higher temperature. Thus, the shoulder at a temperature in the range of 155 °C–157 °C was ascribed to the reduction of RuO₂ particles formed inside the nanotubes [30]. For the Ru/HNT(2) catalyst, the peak broadening at about 120 °C as well as a small shoulder in the TPR-H₂ profile for the Ru/HNT(3) may correspond to the reduction of either agglomerated or physically adsorbed RuO₂ nanoparticles. For the MCM-41/HNT-based catalyst, with a low Ru content the peak in the TPR-H₂ profile was the same as for the HNT-templated counterpart. Thus, it should be concluded that the Ru nanoparticles were located preliminary outside the mesopores. When the Ru content increased, peaks in the TPR-H₂ profile held stable and the peaks were symmetrical but broadened. The shoulder at 130 °C was ascribed to the Ru nanoparticles physically adsorbed outside of both the MCM-41 and the HNTs pores [52]. Meanwhile, for the Ru/MCM-41/HNT(3) sample it may have been caused by particle agglomeration. On the right side from the mean center of the curve, at 165 °C the reduction of the support's surface.

The catalytic properties of the samples obtained were compared for the hydrogenation of benzene. They were evaluated as the specific activity (A_{sp}) calculated from initial activity (mol (benzene)/mol Ru per hour) and the final benzene conversion at the end of the test (180 min). The results for the hydrogenation of benzene are summarized in Figure 4 and Table 2. Cyclohexane was the only product of benzene hydrogenation over all the Ru/HNT and Ru/MCM-41/HNT catalysts.

As depicted in Figure 4, the final benzene conversion over the catalysts based on MCM-41/HNT was higher in all the tests excluding the samples with 3%wt. Ru content. Meanwhile, the Ru/HNT(2) and the Ru/HNT(3) samples had comparable specific activities with those obtained in the composite-based counterparts (Table 2). It may be due to the partial Ru agglomeration on the external surface of HNTs being more available for benzene molecules, while for MCM-41/HNT-supported catalysts the Ru nanoparticles were incorporated into a well ordered silica porous system, which needed time for the diffusion of reagents to the active sites (Figure 1). For the Ru/HNT(2) and the Ru/MCM-41/HNT(2) composites the specific activities were 1856 and 2079 h^{-1} , respectively, while the final benzene conversion over the halloysite-based catalysts was lower compared to the composite-supported ones. In the case of the Ru/MCM-41/HNT(3) and the Ru/HNT(3) catalysts, the ruthenium nanoparticles were partially deposited in the lumen of the halloysite leading to their comparable activity (1535 vs. 1492 h⁻¹). This difference in activities may have been caused by the lower dispersion of the active phase over the surface of the MCM-41/HNT composite, having the high content of large Ru nanoparticles. Ru/MCM-41/HNT(1), with an average particle size of 3.4 ± 0.1 nm being uniformly distributed over the surface of mesoporous aluminosilicate support, was the most active with $A_{sp} = 5594 h^{-1}$ (Figure 4a, Table 2). Thus, benzene conversion over this catalyst exceeded 90% in 45 min and attained 100% in 90 min. This tendency was maintained for the calculated specific normalized activity (Table 2).



Figure 4. Benzene hydrogenation over the HNTs and the MCM-41/HNT-supported Ru catalysts (temperature 80 °C, hydrogen pressure 3MPa, H₂/substrate molar ratio of 3.3). (a) Ru/HNT(1) and Ru/MCM-41/HNT(1), (b) Ru/HNT(2) and Ru/MCM-41/HNT(2), (c) Ru/HNT(3) and Ru/MCM-41/HNT(3).

Sa	mple	A _{sp} , h ⁻¹	A_{spn} *, mol·m ⁻² ·h ⁻¹	Final Benzene Conversion, %	
Fresh	Ru/HNT(1)	4610	0.34	92	
	Ru/HNT(2)	1856	0.16	96	
	Ru/HNT(3)	1492	0.17	100	
	Ru/MCM-41/HNT(1)	5594	0.39	100	
	Ru/MCM-41/HNT(2)	2079	0.22	100	
	Ru/MCM-41/HNT(3)	1535	0.17	100	
After 3rd recycle	Ru/HNT(1)	1986	n.a.	71	
	Ru/HNT(2)	1680	n.a.	74	
	Ru/HNT(3)	580	n.a.	75	
	Ru/MCM-41/HNT(1)	4667	n.a.	95	
After 1st recycle	Ru/MCM-41/HNT(2)	2064	n.a.	98	
	Ru/MCM-41/HNT(3)	1384	n.a.	99	

Table 2. Catalytic properties of the fresh and recycled Ru-catalysts based on the HNT and the MCM-41/HNT composite.

* calculated from Ru average particles size for the bimodal distribution.

As mentioned above, the most active catalysts were Ru/MCM-41/HNT(1) and Ru/HNT(1) with $A_{spn} 0.39$ and $0.34 \text{ mol}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, respectively.

It should be noted that for ruthenium catalysts based on MCM-41/HNT composite (samples 2 and 3), the decrease in the Asp and Aspn (Asp normalized per ruthenium specific surface area) parameters was close (24% and 26%, respectively), which was caused by the similar average NPs diameters, while the Ru content became the major factor influenced by catalytic activity (Tables 1 and 2). In the case of Ru/HNT(2), it was calculated that A_{sp} as well as A_{spn} decreased more than twice as compared to the Ru/HNT(1) counterpart. As for Ru/HNT(2) and Ru/HNT(3), the A_{spn} parameters were close, while Asp was reduced by 20%, confirming the negative enlargement effect of nanoparticles on a decrease in catalytic activity [53].

For the supported metal catalysts, stability, as well as selectivity and activity, are the key factors for its further industrial application. From this point of view, we performed stability tests under the same conditions as compared to the fresh catalysts. As depicted in Figure 5a–c, after recycling, the activity of HNT-based catalysts decreased. It should be noted that the greatest reduction in activity occurred after the first cycle for all the catalysts probably caused by the ruthenium leaching. After the first cycle, the ruthenium content decreased by more than 10% from its initial value and remained practically unchanged for the second and third cycles (Table 1). It was also proved by similar kinetic curves for all the Ru/HNT catalysts, in addition to the final benzene conversions almost being the same (70%–80 %) (Figure 5a–c, Table 2).



Figure 5. Recycle tests for the HNT-supported Ru catalysts (temperature 80 °C, hydrogen pressure 3MPa, H₂/substrate molar ratio of 3.3). (a) Ru/HNT(1), (b) Ru/HNT(2), (c) Ru/HNT(3).

Another finding was observed for the catalysts supported on the MCM-41/HNT composite. For all the samples, partial leaching with lower rates compared to the HNT-supported systems was found (Table 1). This may be due to the hierarchical structure and high specific surface area of MCM-41/composite-based catalysts, which resulted in the stabilization of ruthenium nanoparticles within the porous system. As a result, the specific catalytic activity and the final benzene conversion for Ru/MCM-41/HNT(1) after three cycles were comparable with those obtained on the fresh Ru/HNT(1) (Table 2, Figures 5 and 6).



Figure 6. Recycle tests for the MCM-41/HNT-composite supported Ru catalysts (temperature 80 °C, hydrogen pressure 3MPa, H₂/substrate molar ratio of 3.3). (a) Ru/MCM-41/HNT(1), (b) Ru/MCM-41/HNT(2), (c) Ru/MCM-41/HNT(3).

Finally, we compared the best Ru/HNT(1) and Ru/MCM-41/HNT(1) catalysts with the other systems represented in the literature for benzene hydrogenation (Table 3). As can be seen from Table 3, the specific catalytic activities of the investigated catalysts were much higher compared to the other ruthenium-containing catalysts, based on their supports of a different nature, reported in the literature.

Sample	TOF, h ⁻¹	Ru, wt%	Benzene/Ru Molar Ratio	Benzene Conversion, %	Time, Min	Sel. to Cyclohexane	Temperature, °C;	P(H ₂), MPa	Reference
Ru/C	1600	4.9	2000	100	75	100	110	4	[54]
Ru/Al ₂ O ₃	1416	4.0	1400	100	60	100	80	2	[55]
Ru/CNTs	649	4.0	500	53	60	98	70	1	[56]
Ru/montmorillonite	270	0.83	275	100	60	100	100	3,5	[57]
Ru/PAFs	1600	4.83	2000	79	60	100	80	3.3	[58]
Ru/MOFs	3478	5.0	8000	100	135	100	160	6	[59]
Ru/TEGO*	1302	4	500	75	30	100	70	1	[9]
Ru/hydrotalcite	1300	1	1300	100	60	100	120	6	[60]
Ru/HNT(1)	4610	0.74	2200	92	90	100	80	3	this work
Ru/MCM-41/HNT(1)	5594	0.74	2300	100	75				

Table 3. Comparison of the activity for Ru/HNT(1) and Ru/MCM-41/HNT(1) with the different catalysts reported in the literature.

* TEGO-thermally exfoliated graphite oxide.

It can be concluded that catalysts based on mesoporous MCM-41/HNT have both the higher hydrogenation activity and stability in benzene hydrogenation to cyclohexane. Most probably, it is caused by the extremely high specific surface area of the MCM-41/HNT support as compared with the HNT (as high as 5–8 times, see Table 1). It should be also noted that for all samples based on HNT, as well as on MCM-41/HNT, the higher is metal loading is, the more the catalytic activity decreases. The higher hydrogenation activity of the catalysts with Ru-loading < 1 wt% is explained by the forming of highly dispersed metal particles on the carrier surface. In the case of Ru-loading in the range of 1.3–3 wt%, the metal particles are larger within the partial agglomeration and the distribution thereof is non-uniform (Figure 1). When the metal content is high, the Ru crust forming egg-shell may occur resulting in the blockage of active sites, and the catalysts' specific activity decreasing.

3. Materials and Methods

3.1. Chemicals

The following chemicals were used for the synthesis of catalysts and as reference compounds for the gas chromatography analysis: ruthenium (III) chloride (high purity grade, Aurat, Moscow, Russia), halloysite nanoclay (≥98%, Sigma-Aldrich, St. Louis, MO, USA), hexadecyltrimethylammonium bromide (≥98%, Sigma-Aldrich, St. Louis, MO, USA), tetraethyl orthosilicate (≥98%, Sigma-Aldrich, St. Louis, MO, USA), benzene (≥99%, chemical grade, ECOS-1, Moscow, Russia), cyclohexane (for gas chromatography, Supelco, St. Louis, MO, USA), boric acid (purum, ChemMed, Moscow, Russia).

Double distilled water, ethanol and isopropanol (Reachim, Purum, Moscow, Russia) were used as solvents, and ammonia hydroxide (~25%, ECOS-1, Moscow, Russia) was used for adjusting the pH in the MCM-41/halloysite synthesis.

3.2. The Synthesis of Catalysts

The ordered mesoporous composite MCM-41/HNT was prepared by the template synthesis, using CTAB as a structure-directing agent for the MCM-41 phase formation [49,61]. The ruthenium deposition was performed by the incipient wetness impregnation technique under microwave irradiation as follows. MCM-41/HNT (1 g) powder was dispersed in a water solution (40 mL) of RuCl₃ in the required amount to obtain appropriate metal loading. The dispersion obtained was placed in an ultrasonic bath for 30 min followed by microwave irradiation (800 W) for 3 min and centrifugation (7000 rpm for 2 min). The precipitate was separated and treated with an aqueous solution (30 mL) of NaBH₄ (0.5 M) for the ruthenium reduction. The resulting materials were washed with distilled water, separated via centrifugation and dried at 60 °C for 24 h. The finished solid catalysts were grinded into powder and denoted as Ru/MCM-41/HNT(1), Ru/MCM-41/HNT(2) and Ru/MCM-41/HNT(3) according to their ruthenium content. The ruthenium deposition over the HNTs was performed by the intrinsic wetness procedure under microwave irradiation described in [8,19,20,35].

3.3. Analyses and Instrumentations

The ruthenium content was determined using an ARL Perform'X X-ray fluorescence spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The analysis was performed in vacuum using the UniQuant (Thermo Fisher Scientific, Waltham, MA, USA) program without a standard. Before the analysis, the sample was pressured in tablets with boric acid.

Transmission electron microscopy (TEM) images were obtained on a Jem-2100 (JEOL, Tokyo, Japan) microscope with an accelerating voltage of 100 kV. The sample analyzed was ultrasonically dispersed in ethanol. The particle size distribution was obtained by a statistical evaluation of around 1000 particles from different areas of a number of various TEM images using Image-Pro Plus 6.0 software.

The textural properties of the synthesized and catalyst materials, such as the specific surface area (S_{BET}), volume (Vp) and diameter (Dp) of the pores were determined by a low temperature nitrogen adsorption/desorption technique using a Gemini VII 2390t (Micromeritics Instrument Corp., Norcross, GA, USA) instrument at a temperature of 77 K. Before measurements, the samples were outgassed in vacuum at 300 °C for 4 h. The specific surface was calculated according to the Brunauer–Emmett–Teller (BET) equation in a relative pressure range from 0.04 to 0.25 of the adsorption data. The volume of the pores and their diameter were estimated in terms of the Barrett–Joyner–Halenda model (data obtained from the desorption branch of the isotherm).

Temperature-programmed reduction with hydrogen (TPR-H₂) was performed with a AutoChem 2950HP instrument (Micromeritics Instrument Corp., Norcross, GA, USA). Before the analysis, the catalyst (100 mg) was pretreated at 400 °C for 30 min under air flow to oxidize the ruthenium nanoparticles. Then, a sample was purged with Ar flow at 400 °C for 1 h, cooled to 50 °C. The reduction step was performed under the 30 mL/min flow of 8 vol.% H₂–92 vol.% Ar mixture in the range

of 50 °C–400 °C with a ramp of 10 K/min. The consumption of H_2 and the ruthenium content were calculated using the AutoChem HP V2.04 program (Micromeritics Instrument Corp., Norcross, GA, USA).

3.4. Catalytic Experiments

The catalytic activity in benzene hydrogenation was evaluated in a Parr 5000 Multiple Reactor System (Parr Instruments, Frankfurt am Main, Germany) with stainless steel batch reactors having a Teflon inlet and a magnetic stirrer. The reactor was loaded with benzene (0.01 moles) without any solvent and 60 mg of the catalyst, purged with hydrogen and then pressurized. The catalytic tests were run with 1500 rpm stirring at a hydrogen pressure of 3.0 MPa and a temperature of 80 °C. After reaction, the reactor was cooled down to room temperature, the pressure was dropped to atmospheric and the catalyst was removed from the reaction products via centrifugation, washed 3 times with 10 mL of ethanol and dried at 60 °C for 24 h. The recycling tests were performed under the same conditions as for fresh catalysts. The hydrogenation products were analyzed in isotherm (110 °C) using a Chromos GC-1000 gas chromatograph (Chromos Engineering, Dzerjinsk, Russia) equipped with a flame-ionization detector and a capillary column MEGA-WAX Spirit (MEGA, Legnano, Italy).

The specific catalyst's activity in hydrogenation (A_{sp}, h^{-1}) was calculated as the amount of reacted benzene (Nb*Cb) per mole of ruthenium and the time in hours, according to the formula:

$$A_{sp} = \frac{N \times Cb}{m_{cat} \times \frac{\omega_{Ru}}{M_{Ru}} \times t_i},$$

where Nb—moles of benzene, Cb—benzene conversion, m_{cat} —the catalyst weight, ω_{Ru} —ruthenium content determined by XRF, M_{Ru} —ruthenium molar mass and t_i is the time for which the benzene conversion (Cb) was evaluated.

The specific catalyst's activity normalized per ruthenium specific surface area (A_{spn}) was calculated as follows:

$$A_{\rm spn} = \frac{A_{\rm sp}}{S_{\rm sp} \times M_{\rm Ru}},$$

where A_{sp}—specific catalyst's activity and S_{sp}—ruthenium specific surface area, calculated as:

$$S_{sp} = \frac{6}{d \times \rho_{Ru}}$$

where d—average nanoparticle diameter, ρ —metal density, and k—shape factor (6 for spherical nanoparticles).

Each experiment was carried out three times under the same conditions, with the results differing by no more than 2% from the corresponding average value. The measurement error did not exceed 1%.

4. Conclusions

Mesoporous ruthenium catalysts (0.74–3.06 wt%), based on ordered MCM-41 silica arrays on aluminosilicate halloysite nanotubes (HNTs), as well as HNT-based counterparts, were synthesized and tested in benzene hydrogenation. The TEM and low-temperature nitrogen adsorption/desorption analyses for the HNT core-shell silica composite-supported Ru catalysts proved the well ordered mesoporous silica structure of the MCM-41 type assembled on the outer surface of the HNTs and retained after Ru loading. According to calculations based on the TEM results, the higher the metal loading, the higher the sizes of the particles formed by both the MCM-41/HNT and the HNT-based catalysts. The latter ones had particles varying from 3.6 to 5.4 nm in diameter, located predominantly on the outer surface of the HNTs. For the MCM-41/HNT-supported ones, at higher metal content the particle size distribution became bimodal, and particles with more than 6.7–7.2 nm in diameter formed.

When the metal loading increased, the Ru nanoparticles both intercalated into the MCM-41/HNT porous system and agglomerated outside the mesopores.

For all samples based on HNT, as well as on MCM-41/HNT, the higher is metal loading was, the more the specific catalytic activity decreased. The higher hydrogenation activity of the catalysts with Ru loading < 1 wt% was explained by the formation of metal particles highly dispersed over the surface of the MCM-41/HNT composite. The Ru/MCM-41/HNT(1) catalyst with an average particle size of 3.4 ± 0.1 nm, being uniformly distributed over the surface of the mesoporous aluminosilicate support, was the most active in the hydrogenation of benzene to cyclohexane and the specific activity of 5594 h⁻¹ was achieved with A_{spn} 0.39 mol·h⁻¹·m⁻². For catalysts based on the MCM-41/HNT composite with a higher Ru content, the decrease of the A_{sp} and A_{spn} parameters was close, which was caused by similar average NPs diameters, while the Ru content became the major factor influenced by catalytic activity. As for the Ru/HNT(2) and Ru/HNT(3), the A_{spn} parameters were close, while the A_{sp} was slightly reduced by 20%, confirming the negative enlargement effect of nanoparticles on a decrease in catalytic activity.

The MCM-41/HNT composite-supported Ru catalysts were found to be more stable under recycling due to hierarchical structure and a high specific surface area, resulting in the stabilization of the ruthenium nanoparticles within the porous system. As a result, the specific catalytic activity and final benzene conversion for Ru/MCM-41/HNT(1) after 3 cycles were comparable for those obtained with the fresh Ru/HNT(1).

These catalysts, based on a synergistically strong, new type material, consisting of synthetic mesoporous silica of MCM-41 type arrays on natural clay nanotubes, are safe, environmentally friendly materials and could be easily scaled up for industrial application.

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