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Bulletin of Chemical Reaction Engineering & Catalysis, 10 (3), 2015, 313-323

Research Article

Influence of the Mesoporous Polymer Matrix Nature on the Formation of Catalytically Active Ruthenium Nanoparticles

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Received: 27th July 2015; Revised: 4th December 2015; Accepted: 5th December 2015

Abstract

This paper reports on ruthenium nanoparticles formation and stabilization by hypercrosslinked polystyrene and the catalytic properties of the nanocomposites obtained. Hypercrosslinked polystyrene with functional groups and without them was used. The nanocomposites were characterized using low-temperature nitrogen physisorption, X-ray photoelectron spectroscopy and transmission electron microscopy. It is established that the tertiary amine group of the support influences both formation of ruthenium nanoparticles, and their catalytic properties in the selective hydrogenation of D-glucose. ©2015 BCREC UNDIP. All rights reserved.

Keywords: Ruthenium Nanoparticles; Mesoporous Polymer Matrix; Hypercrosslinked Polystyrene; Tertiary Amine Group; Hydrogenation of D-glucose

How to Cite: Sulman, M., Doluda, V., Grigoryev, M., Manaenkov, O., Filatova, A., Molchanov, V., Sidorov, A., Bykov, A., Shkileva, I., Sulman, A., Stein, B., Matveeva, V. (2015). Influence of the Mesoporous Polymer Matrix Nature on the Formation of Catalytically Active Ruthenium Nanoparticles. *Bulletin of Chemical Reaction Engineering & Catalysis*, 10 (3): 313-323. (doi:10.9767/bcrec.10.3.8824.313-323)

Permalink/DOI: http://dx.doi.org/10.9767/bcrec.10.3.8824.313-323

1. Introduction

The metal nanoparticles (NPs) possess unique catalytic properties due to their large surface area and considerable number of surface atoms leading to an increased amount of active sites [1-3]. The catalytic properties of metal NPs depend on their size, size distribution, and environment [4]. Moreover, the surface of nanoparticles plays an important role in the catalysis, being responsible for their selectivity and activity. As was demonstrated earlier, the formation of NPs in a nanostructured polymeric environment allows enhanced control over nanoparticle characteristics, yet the stabilizing polymer (its functionality) is of great importance, determining the state of the nanoparticle surface [5-9]. Controlled growth of metal

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NPs in a mesoporous polymer matrix is possible if it occurs in cavities or pores. In this case, the size of the growing particles can be limited to the cavity size [10]. Hypercrosslinked polymeric matrices are prospective organic supports for metal NPs synthesis and stabilization [11, 12] due to the large specific surface area (usually near 1000 m^2/g) and relative thermal stability [13]. Hypercrosslinked polystyrene (HPS) is the first representatives of such polymeric matrices [14]. Due to high crosslinking density, which can exceed 100 %, HPS consists of nanosized rigid cavities (pores), the sizes of which depend on the way of HPS preparation. Besides, HPS has the ability to swell practically in any liquid medium including poor solvents for polystyrene.

Hydrogenation of saccharides is an important reaction for the synthesis of sugar alcohols, which could be used as intermediates in the production of pharmaceuticals, as well as artificial sweeteners. Moreover, synthesized polyols can play a key role in the production of biofuels from renewable sources [15]. The most important saccharide hydrogenation processes are glucose, xylose, maltose, and lactose hydrogenation to the corresponding alcohols [15-19]. The catalytic method of D-glucose hydrogenation to D-sorbitol is a complex process (Figure 1) providing several reaction routes. This process is of great industrial importance because D-sorbitol is a valuable additive in foods, drugs, and cosmetics. Moreover, D-sorbitol is an intermediate in Vitamin C production [20].

The use of heterogeneous systems for the selective hydrogenation of D-glucose is of great practical importance considering its high efficiency, simplicity of technological support, cost minimization, and relative ecological safety [21-23]. Now the industrial catalyst for D-glucose hydrogenation is Raney-type Ni [24-26]. However, the drawback of Ni catalysts is their tendency to Ni leaching that results not only in the loss of catalytic activity (after five

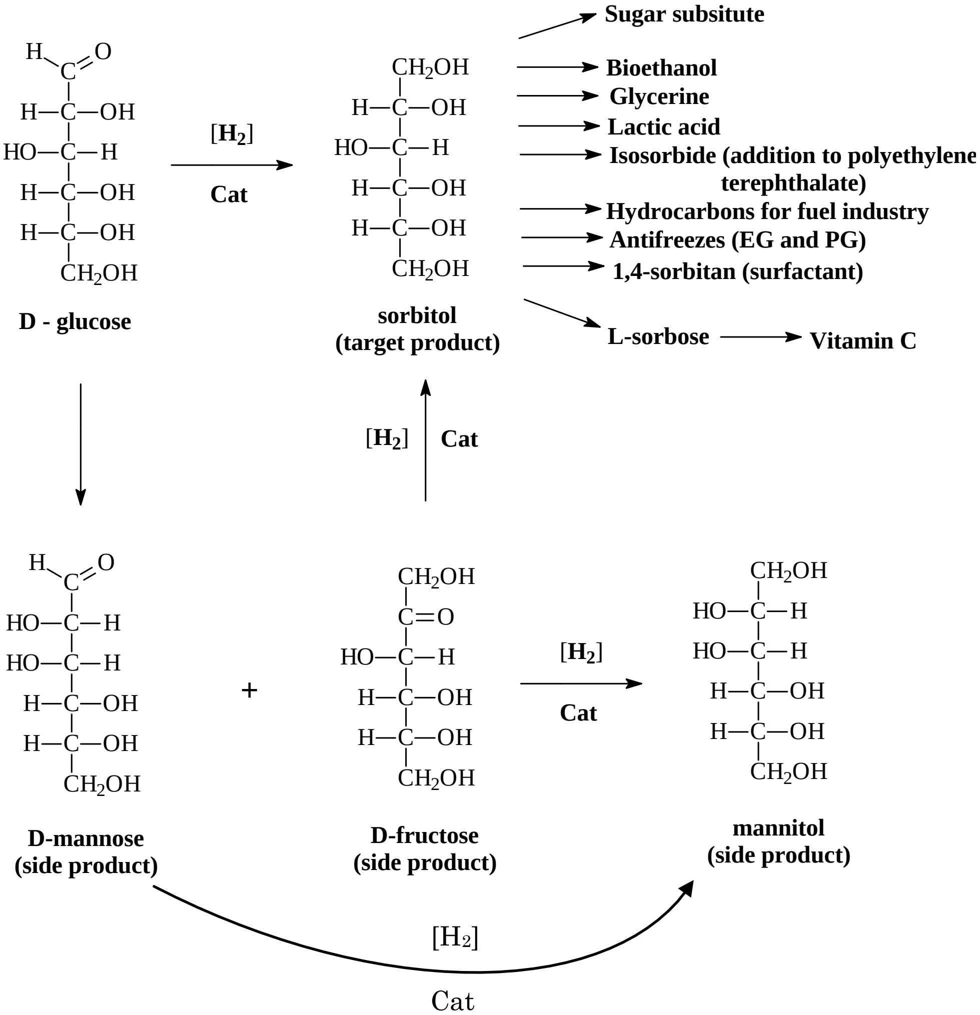

Figure 1. Scheme of possible reaction products in D-glucose hydrogenation

recycles the activity decreases by 40%) but also to the pollution of target product [20]. Moreover, the purification of D-sorbitol is necessary, because the maximum allowable concentration of Ni is 2 mg/kg for the food industry [27]. The use of ruthenium catalysts could circumvent this problem, since ruthenium is stable against leaching [28, 29]. The catalysts on the base of ruthenium [24, 28] occupy the leading position in the activity among the metals Ru > Ni > Rh > Pd [29] and it simplifies considerably the technology of obtaining D-glucose. Ru nanoparticles supported on mesoporous silicas [30-32], porous carbons [25, 28, 29], zeolite β [33], alumina [26] and others have been reported to be highly active in various reactions.

The main idea of our investigations is the use of HPS for the metal NPs synthesis. This material can act as a nanostructured matrix which governs the metal particle growth. As we demonstrated earlier, HPS perfectly controls the formation of Co- [34], Pt- [35, 36], Pd- [37] and Ru-NPs [38]. These NPs showed excellent activity and selectivity in the reaction of fine organic synthesis. Nowadays, commercially fabricated HPS can combine micro-, meso-, and macropores allowing better mass transfer of reagents due to large pores.

In this paper, we reported the comparison of the Ru nanoparticles synthesized on HPS with functional groups and without them. Ru-NPs physicochemical characterization and their catalytic properties in the reaction of D-glucose selective hydrogenation are also discussed.

2. Materials and Method

2.1. Material

Hypercrosslinked polystyrene Hypersol-Macronet MN100 (functional group-tertiary amine, designated as MN100) and Hypersol-Macronet MN270 (functional group-none, designated as MN270) were purchased from Purolite International Ltd., U.K. The size of the MN100 and MN270 granules is 50-70 µm. The schematic images of different type of HPS and the photos of the support samples are presented in Figure 2. The granules were washed with acetone and water twice and dried under vacuum for 24 h. Ruthenium(IV) hydroxychlo-

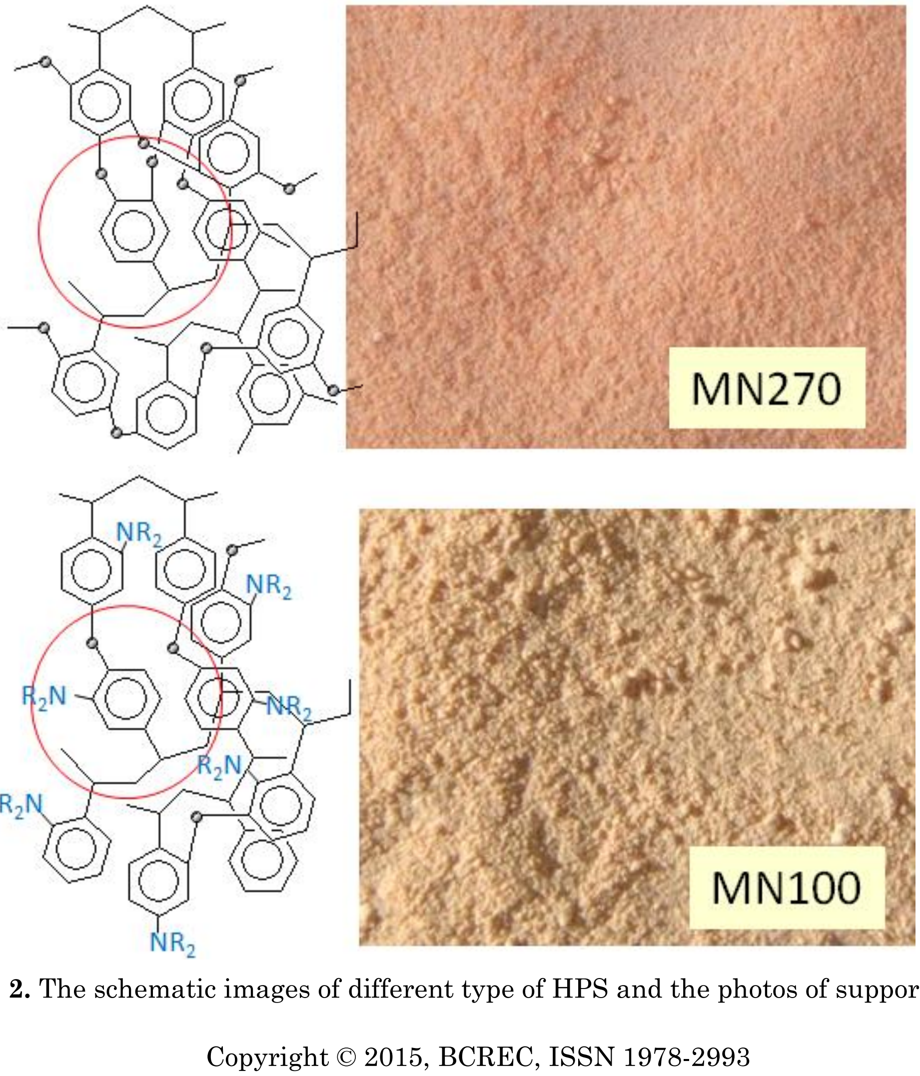

Figure 2. The schematic images of different type of HPS and the photos of support samples

ride (Ru(OH)Cl_3 (pure, OJSC Aurat, Russia), tetrahydrofuran (THF) (98.0%, Sigma-Aldrich), methanol (MeOH) (99.0%, Sigma-Aldrich), sorbitol and D-glucose (Aldrich (USA and Germany) were used as received. Distilled water was purified with the Elsi-Aqua (ELSICO Ltd., Moscow) water purification system.

2.2. Synthesis of Ru nanoparticles

For the synthesis of Ru nanoparticles based on such types of Hypersol-Macronet as MN100 and MN270 were used. Ruthenium catalysts were synthesized by wet impregnation. In a typical experiment 3 g of MN100 or MN270 (pretreated and dried) was impregnated with Ru(OH)Cl_3 dissolved in 6 mL of a solvent mixture (H_2O, MeOH and THF in the ratio of 1:1:4) for 10 min. Then the Ru-containing polymer was dried at 75 ± 2 °C during 1 h and boiled for about 2 h in 21 mL of 0.1 M NaOH solution with the addition of 2 mL of hydrogen peroxide (30%). After that the Ru-containing polymer was washed with water until pH 6.4–7.0 and the absence of reaction on chloride ions, then it was dried again at t = 75 ± 2 °C. The reduction with hydrogen gas was carried out at atmospheric pressure and a temperature of 300 °C for 2 h then it was cooled to ambient temperature in a nitrogen atmosphere. Thus we synthesized Ru-containing catalysts with Ru loading of 3 % (Ru/MN100 and Ru/MN270).

2.3. Characterization of Ru nanoparticles

The specific surface area, pore size distribution of the supports and the Ru-containing catalysts were investigated by physical adsorption of nitrogen using BECMAN COULTERTM SA 3100TM (Coulter Corporation, Miami, Florida), BECMAN COULTERTM SA-PREPTM (Coulter Corporation, Miami, Florida), and electronic balance GX-200 (A&D Company, Limited, Tokyo, Japan). The following analysis conditions were used: t = -196 °C, relative pressure 0.9814 (for the pores less than 100 nm), PSD (ADS) profile.

X-Ray photoelectron spectroscopy (XPS) was carried out using Mg Ka (*hv* = 1253.6 eV) radiation with ES-2403 spectrometer (provided by the Institute for Analytic Instrumentation of the Russian Academy of Sciences, St. Petersburg, Russia) equipped with energy analyzer PHOIBOS 100-MCD5 (SPECS, Germany). All the data were acquired at X-ray power of 100 W. The survey spectra were recorded at a step of 0.5 eV with an analyzer pass energy 40 eV, and high resolution spectra were recorded at a step of 0.05 eV with an analyzer pass energy 7 eV. The samples were allowed to outgas for 60 min before the analysis and were sufficiently stable during the examination.

Transmission electron microscopy (TEM) was carried with a JEOL JEM1010 instrument at electron accelerating voltage of 80 kV. The samples were prepared by embedding Ru/MN100 or Ru/MN270 samples in epoxy resin with following microtomming at ambient temperature. The images of the resulting thin sections (ca. 50 nm thick) were collected with the Gatan digital camera and analyzed with the Adobe Photoshop software package and the ImageJ software.

The size, form and internal structure of HPS granules were determined by the method of the Scanning Electron Microscope (SEM) on a microscope of FIB Quanta 200 3D at the accelerating voltage of 30 kV with the permission ~ 2 nm.

2.4. Testing of catalytic properties of Ru nanoparticles

The catalytic properties of the Ru catalysts for D-glucose hydrogenation were evaluated using a 150 mL stainless-steel autoclave reactor (Figure 3). The suspension of a heterogeneous catalyst with the solvent was introduced into the autoclave through the side fitting and the substance under study dissolved in 15 mL of solvent into the loading chamber. The total volume of the liquid fraction was 50 mL. Before the reaction the catalyst was saturated with hydrogen at a preselected temperature for 30 min, and then the substrate was introduced. The process of hydrogenation was carried out at constant shaking of the autoclave. The product liquid in the reactor was analyzed by the method of HPLC, using a refractometric detec-

Table 1. Pore structure parameters of support

Support	Total surface area, m^2/g	Surface area of micropores, m^2/g	Total pore volume, mL/g	Micropore pore volume, mL/g	Pore size, nm
MN 100	720	600	0.48	0.22	< 10
MN 270	1370	1120	0.79	0.32	< 10

tor. Reprogel-H column: 500×10 mm, the number of theoretical plates 160000; conditions of separation: eluent consumption (9 Mmol solution H_2SO_4) 0.5 mL/min; temperature of the column 25 °C; eluent pressure 6.5 MPa; time of analysis 30 min. The qualitative identification was carried out using of pure reference substances.

3. Results and Discussion

The hypercrosslinked polymers, including HPS possess porous structure. In Figure 4 the data of SEM are presented and the internal porous structure of HPS by the example of MN 270 is well visible.

Figure 5 shows N_2 adsorption – desorption isotherms for the catalyst supports used in this work. It can be seen from Figure 5a that the isotherm of support MN100 is of type I with a inclined profile in the adsorption branch and the pore size distribution (PSD) curve (inset), indicating the presence of micro- and mesopores. The isotherm of support MN270 (Figure 5b) is also of type I with a H3 hysteresis loop and PSD demonstrates the presence of both micro- and mesopores. The detailed parameters of the supports are compiled in Table 1, which shows the different pore structure parameters for the supports used in this work. It should be noted that supports have a different surface area but similar porous structure. The results of the method of physical adsorption of nitrogen for both supports showed that more than 50% (vol.) of pores have the pore size less than 10 nm (Table 1). The presence of both micropores and mesopores is important because they can control Ru nanoparticle formation by controlling the volume of the precursor material inside the pores [10].

Figure 6 shows TEM images and the histogram of particle size distribution of Ru/MN 100 (Figure 6a) and Ru/MN 270 (Figure 6b) catalysts. Ru nanoparticles size in case of Ru/MN 100 was about 4 nm and NPs are wide distributed (Figure 6a). For the Ru/MN 270 catalyst, Ru nanoparticles are narrow distributed with mean diameter 1.4 nm (Figure 6b). Thus, in case of the support with tertiary amine groups of a Ru NPs aggregate due to coordination with nitrogen and the size of NPs is more in comparison with the nonfunctionalized support.

To determine the qualitative and quantitative composition of the surface of Ru-containing NPs, stabilized in HPS matrix, the study of the catalysts samples was performed by the method of X-ray photoelectron spectroscopy. Figure 7 shows the XPS spectrum for Ru 3p regions of Ru/MN 100 and Ru/MN 270 (red and green lines accordingly). The spectrum illustrates insignificant differences between peaks of binding energy of Ru $3p_{3/2}$ at 463.4 eV (for Ru/MN 100) and Ru $3p_{3/2}$ at 464.0 eV (for Ru/MN 270). In Table 2, XPS data on qualitative and quantitative composition (atom %) of the surface of Ru-containing nanoparticles, stabilized in different type of HPS are presented. It was established according to the analysis results (Table 2) that ruthenium on the surface is in the form of the mixture of dioxide (Ru(IV))

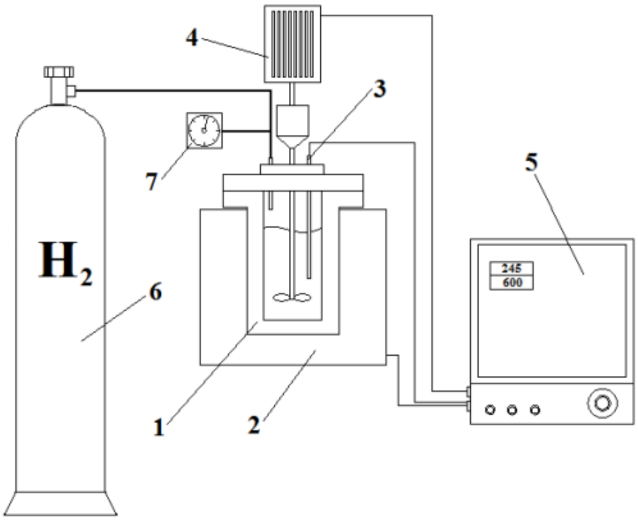

Figure 3. Laboratory setup for cellulose hydrolytic hydrogenation include a high-pressure reactor (1), a heater (2), a thermocouple (3), a stirrer motor (4), a control unit (5), a hydrogen bottle (6), and a manometer

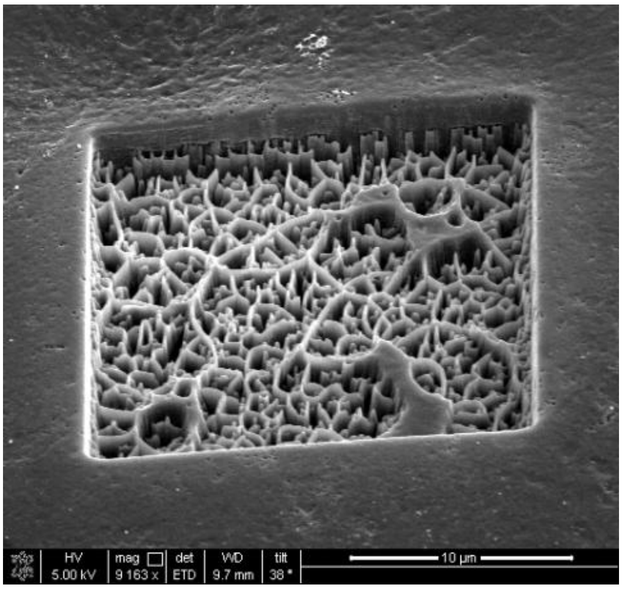

Figure 4. Internal porous structure of HPS by the example of MN 270 (Scanning Electron Microscopy)

with a different degree of hydration with the predominance of the latter. It is supposed that dioxide of ruthenium (Ru(IV)) is the oxidized ruthenium surface (Ru(0)) [39]. The absence of the ruthenate-anion should be noted in case Ru NPs are formed on the support with tertiary amine groups. Figure 8 presents the high resolution spectrum of Ru $3p_{3/2}$ for Ru/MN 100 (Figure 8a) and Ru/MN 270 (Figure 8b) as an example.

The catalytic properties of the catalysts prepared in this work in the liquid-phase of D-glucose hydrogenation were measured and compared with commercial catalyst, and are summarized in Table 3. The turnover frequency (TOF) value (defined as mol D-glucose converted per mol of ruthenium per second) shows that Ru NPs supported on HPS are at least 2-times more active than commercial Ru/C catalyst. It should be noted that the influence of tertiary amine groups of HPS on catalytic properties of Ru NPs results in selectivity increase, whereas the activity is approximately identical for both catalysts (Table 3).

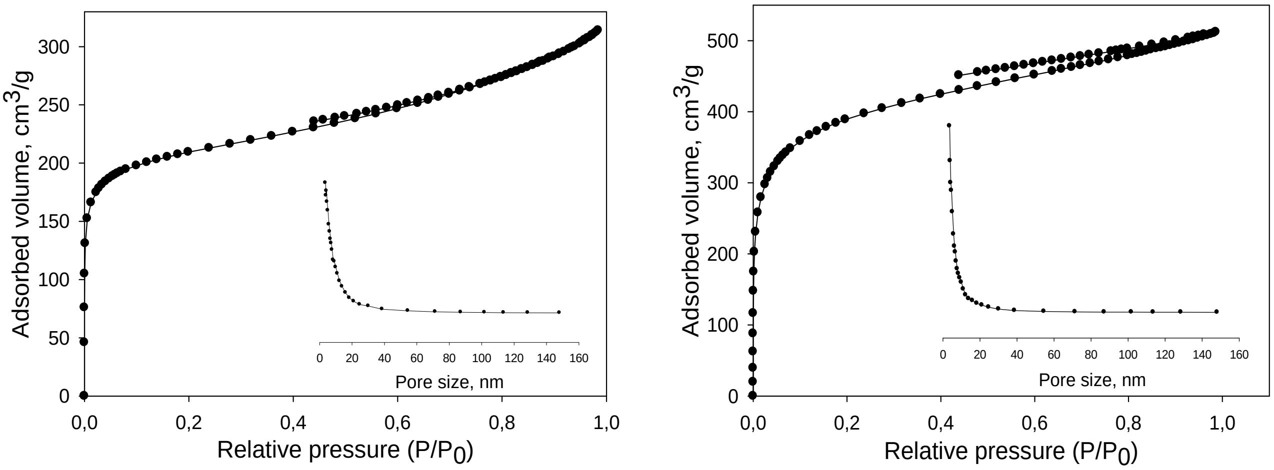

Figure 5. N_2 adsorption – desorption isotherms for the catalyst supports: (a) MN100 and (b) MN270

Table 2. Qualitative and Quantitative Composition of the Surface of Ru-Containing Nanoparticles, Stabilized in different type of HPS, According to XPS Data and the Bond Energy for Ru $3p_{3/2}$

Ru species	Fraction of Ru species (atom%)/(bond energy for Ru $3p_{3/2}$, eV)	
	Ru/MN 100	Ru/MN 270
RuO_2	28.2 (462.6)	22.9 (462.4)
$RuO_2 \times nH_2O$	71.8 (463.5)	58.5 (463.6)
RuO_4^{2-}	0.0	18.8 (465.0)

Table 3. The catalytic properties of the catalysts

Catalyst	Conversion, %	Selectivity, %	TOF, s-1
Ru/MN 100	98	99	0.17
Ru/MN 270	98	96	0.19
Ru/C	97	94	0.09

(Reaction conditions: temperature 413 K, initial H_2 pressure 4 MPa, time 80 min, concentration of D-glucose 1.6 mol/L, concentration of catalyst 2.3×10^{-3} mol/L).

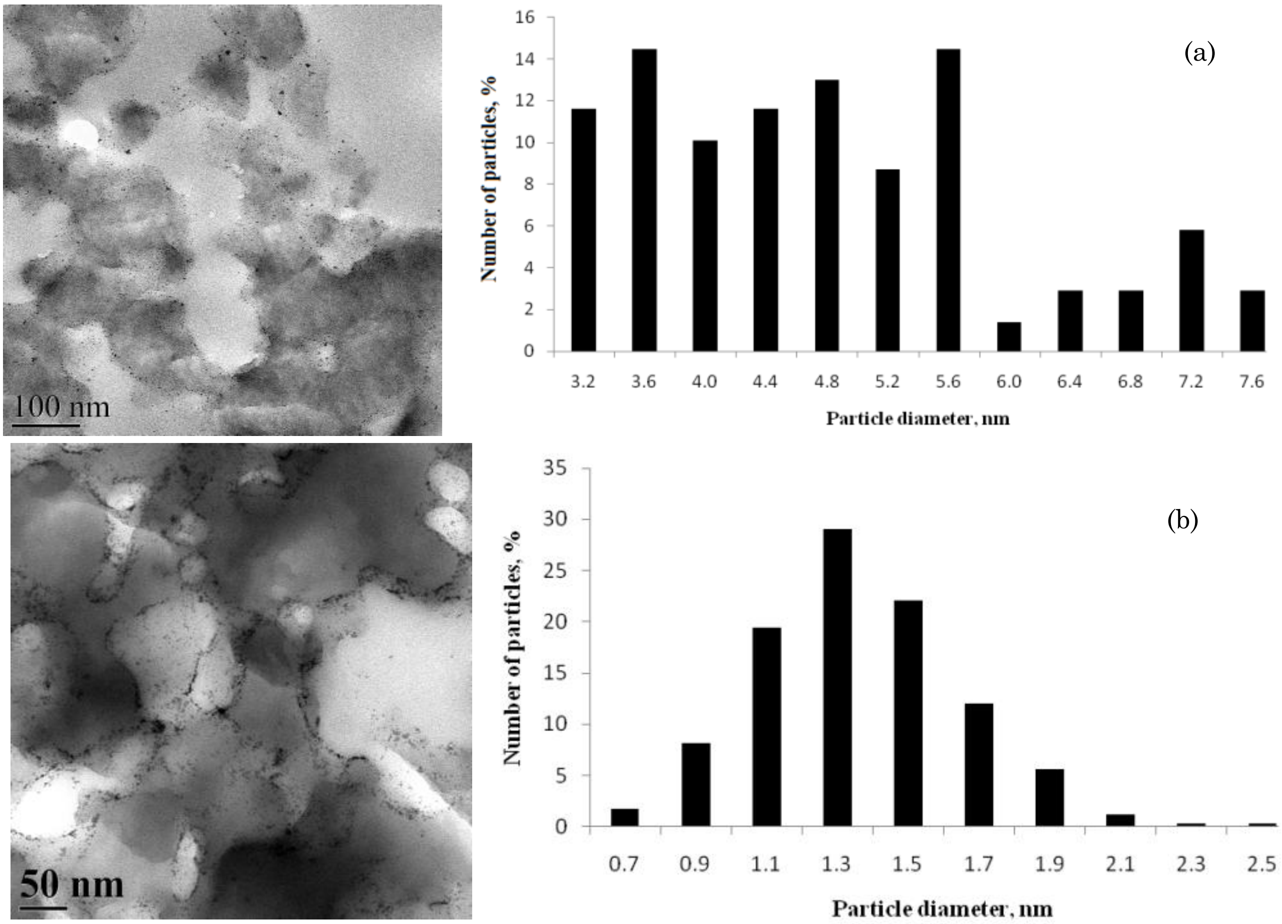

Figure 6. TEM images and the histogram of particle size distribution: Ru/MN 100 (a), Ru/MN 270 (b)

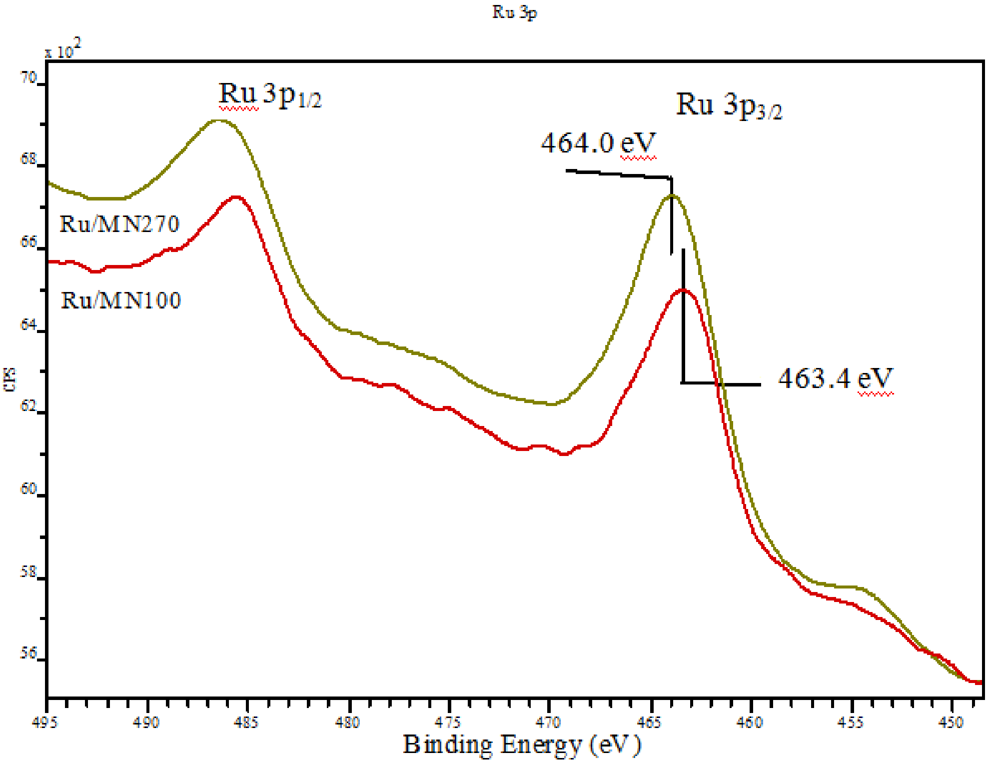

Figure 7. XPS spectrum for Ru 3p regions of Ru/MN 100 and Ru/MN 270 (red and green lines accordingly)

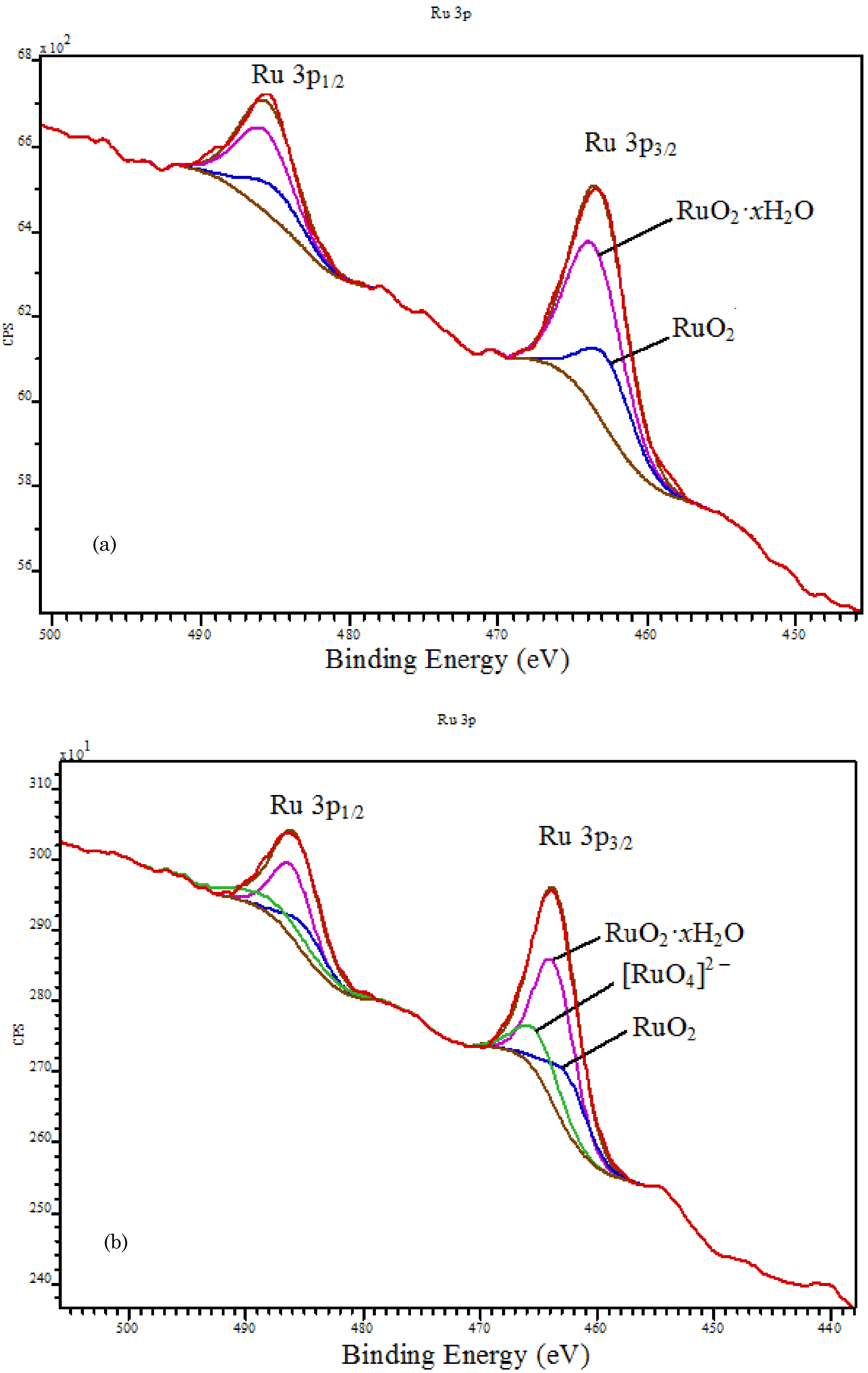

Figure 8. Survey high resolution spectrum of Ru $3p_{3/2}$ for Ru/MN 100 (a) and Ru/MN 270 (b)

4. Conclusions

The presented research showed that the mesoporous polymer matrix nature influences on the formation of catalytically active ruthenium nanoparticles. The comparison of Ru nanoparticles synthesized on HPS with functional groups (tertiary amine) and without them indicated that there is the difference of surface area and similarity of pore structure. Moreover, by TEM it was shown that the presence of tertiary amine groups in the support influences the size of the formed ruthenium nanoparticles. Namely the existence of nitrogen atom in the support promotes the aggregation of Ru NPs. In case of the catalyst Ru/MN 100 the mean diameter of nanoparticles was about 4 nm, whereas for the catalyst (without functional groups) the mean diameter of particles is 1.4 nm. The catalyst Ru/MN 270 showed higher activity in comparison with the catalyst Ru/MN 100 in the reaction of D-glucose selective hydrogenation. The selectivity increasement can be explained with the modification of Ru nanoparticles by nitrogen atoms . Catalysts on the basis of HPS showed activity twice higher in comparison with the commercial catalyst Ru/C.

Acknowledgments

Financial support was provided by the grant of Russian Science Foundation (№15-13-20015), the Ministry of Education and Science of the Russian Federation and the Russian Foundation for Basic Research. The authors thank Dr. Lyudmila Bronstein (Department of Chemistry, Indiana University, United States) for help with TEM studies.

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