



Characterization and thermal stability of ruthenium nanoparticles supported on γ -alumina

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ABSTRACT

Ru/ γ -Al₂O₃ catalyst of 1.1% was prepared by reduction of RuCl₃ in ethylene glycol using a microwave-assisted solvothermal method. Structure of the as-prepared and heated in H₂ at 500–700 °C catalyst samples was studied by XPS, BET, XRD and HRTEM techniques. The catalyst dispersion was determined by various chemisorption techniques and agreement between them was reasonable. The dispersion of fresh catalyst decreased slightly from 0.53 to 0.49 by hydrogen treatment at 700 °C, and good correspondence with HRTEM data was obtained. Results indicate on high stability of the Ru nanoparticles in the low-loaded colloidal Ru/ γ -Al₂O₃ catalyst under reducing conditions.

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1. Introduction

The study of metal nanoparticles on oxide supports is of importance in catalysis because these systems play a central role in industrial processes and in pollution abatement. The mean particle size and particle size distribution of the metal nanoparticles is often critical in determining catalytic activity and selectivity [1]. In recent years, well-defined supported ruthenium nanoparticles were successfully synthesized via controlled colloid chemistry routes [2–10]. According to Galletti et al. [8] the preparation of Ru nanoparticles is difficult and less investigated as compared to Pt [1,11,12] or Pd nanoparticles [12,13]. Frequently, Ru nanosystems were obtained by reduction of RuCl₃ in glycols, such as ethylene glycol in the presence of the inorganic support [2,3,6,9], hydrogen reduction [10] or sodium borohydride reduction [14]. Recently, the colloidal Ru/Al₂O₃ catalysts were prepared by the reduction of RuCl₃ in a low boiling point alcoholic solution under overpressure [8]. In order to stabilize the colloid nanoparticles from agglomeration, metal salts are reduced in the presence of organic compounds as stabilizers [11,12]. Unsupported Ru nanoparticles are also prepared using polymers [15], amines, alcohols or thiols [16,17] and organosilane fragments [18] as stabilizers. However, the protected Ru nanoparticles are not stable under treatment at higher temperature since such treatment leads to a sintering of particles [18,19].

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Supported ruthenium nanoparticles were prepared without using any stabilizing agent [2,3,6,9] or for preventing it from aggregation capping agents such as poly(N-vinyl-2-pyrrolidone) (PVP) [8,20–22] and dendrimers [10] were used. The role of the capping agent in catalytic activity is not well-understood in spite of its importance to model nanoparticle systems for studying heterogeneous catalysis [11]. The removal of PVP from the Ru(PVP)/ γ -Al₂O₃ catalyst is difficult but necessary to obtain active catalytic system [8,21]. Moreover, the removal of ligands or the templating agent also leads to metal sintering. A survey of the literature teaches that, although a growing number of contributions deal with supported colloidal Ru catalysts, no many information is available concerning the resistance towards sintering of such systems at higher temperature. It is important since ruthenium nanocatalysts are attractive for catalytic processes of great industrial interest such as ammonia synthesis [2] or hydrogenation of phenol [8]. Only some authors have reported undesirable ruthenium colloid aggregation during catalytic reactions [23–25].

The present study focuses on the characterization and thermal stability of the colloidal low-loaded Ru/ γ -Al₂O₃ catalyst obtained by the microwave (MW)-assisted synthesis. The catalyst was prepared without using any stabilizing agent. The thermal stability of the supported Ru colloid was evaluated by heating of the as-prepared catalyst in hydrogen at 500–700 °C. Such studies are important since Ru(0) nanoparticles are expected to have a weaker interaction with the support than in the catalysts obtained by the impregnation method [2]. More detailed gas chemisorption (H₂ and O₂), and H₂–O₂ titration studies were also performed. Some inconsistencies exist in literature, especially with using of

the O₂ chemisorption and H₂–O₂ titration method for characterization of the traditional Ru catalysts.

2. Experimental

Synthesis of the colloidal 1.1 wt.% Ru/ γ -Al₂O₃ catalyst was similar to that described for the 5.1% Ru/ γ -Al₂O₃ catalyst [6,9]. The support was prepared by hydrolysis of aluminum isopropoxide followed by calcination in air at 550 °C. First, ruthenium chloride was dissolved in ethylene glycol (EG) and then γ -Al₂O₃ was added to form a suspension. The mixture was stirred for 15 min at room temperature and then the microwave-solvothermal reduction was carried out at 200 °C for 20 min in a reaction system MW Reactor Model 02–02 (ERTEC, Poland). The mixture was then cooled down in an ice-water bath. Most of the ethylene glycol and another organic products was removed by washing of the obtained solid with a NaNO₃ solution and then with distilled water to remove Na and Cl ions. Next, the Ru/ γ -Al₂O₃ catalyst was dried under vacuum at RT. Part of this catalyst was heated in hydrogen flow at 500–700 °C (5 °C/min) for 5 h to study thermal stability of the ruthenium colloid supported on γ -Al₂O₃.

The ruthenium content in the catalyst was estimated by ICP-AES method. The BET surface areas were determined from the nitrogen adsorption using a volumetric glass apparatus (base pressure 10^{−6} Torr). The same apparatus was used to perform H₂ and O₂ chemisorption, and H₂–O₂ titration measurements. Before adsorption, the catalyst was in situ heated in H₂ at 400 °C for 2 h and evacuated at the same temperature for 2 h. The total and reversible H₂ uptakes were determined at 100 °C, as described in [6,9]. Next, the sample was evacuated at 400 °C for 2 h, cooled under vacuum to 0 °C and exposed to O₂ for the oxygen adsorption measurements. For the titration, the sample was first evacuated

for 15 min at 0 °C, then isolated from the pumps and the temperature was raised to 100 °C for measurement of the H₂ uptake.

The morphology of the samples was investigated by transmission electron microscopy (TEM) method with Philips CM 20 Super-Twin microscope operated at 200 kV. Images were digitized using a high-resolution CCD camera and computer processed to obtain the fast Fourier transforms (FFT). The size distribution of ruthenium particles and their mean size was calculated using ImageJ program [26]. X-ray powder diffraction (XRD) patterns were obtained employing a DRON-3 diffractometer using Ni-filtered CuK_α radiation. XPS measurements were performed with the same spectrometer as in [6].

3. Results and discussion

3.1. Structure characterization of colloidal Ru/ γ -Al₂O₃ catalyst

In the microwave-polyol method, the reduction of RuCl₃ by ethylene glycol proceeds quickly and Ru adsorbs at the alumina support as neutral nanoparticles rather than as ions. XPS analysis of the as-prepared catalyst confirmed the complete reduction of RuCl₃ to Ru(0) and absence of the chlorine ions on the catalyst surface (XPS spectrum not shown). Table 1 shows that deposition of Ru nanoparticles from the colloidal solution on γ -Al₂O₃ nearly did not change the BET surface area of the support (245.9 m²/g). Only, treatment in hydrogen at 700 °C cause decrease of the catalyst surface area by about 14%. The Ru content in the as-prepared catalyst was 1.1 wt.% and it was slightly lower than the nominal value (1.2 wt.%). XRD patterns of all samples (not shown) contained only peaks from the support, indicating that even after treatment at 700 °C, Ru nanoparticles are either amorphous or highly dispersed, with particle sizes below the detection limit of the XRD technique.

Table 1
BET surface area and adsorption of H₂, O₂ and H₂–O₂ titration on the 1.1% Ru/Al₂O₃ catalyst.

Catalyst treatment	BET surface area (m ² /g)	H ₂ uptake (μmol/g cat)		O ₂ uptake (μmol/g cat)	Exp. H ₂ –O ₂ ^{a,b} (μmol H ₂ /g cat)	Calc. H ₂ –O ₂ ^b (μmol H ₂ /g cat)
		Total	Rev			
As-prepared	251	34.0	5.0	57.0	156.2	148.0
H ₂ , 500 °C	245	33.0	4.5	56.0	152.0	145.0
H ₂ , 600 °C	238	32.0	4.0	55.1	148.0	142.2
H ₂ , 700 °C	215	30.5	3.5	50.0	141.2	130.5

^a H₂ titration at 100 °C after exposure sample to O₂ at 0 °C.

^b Exp., Calc. – experimental and calculated values from the O₂ uptake on a given sample at final pressure of O₂; [2 × (O₂ uptake) + total H₂ uptake].

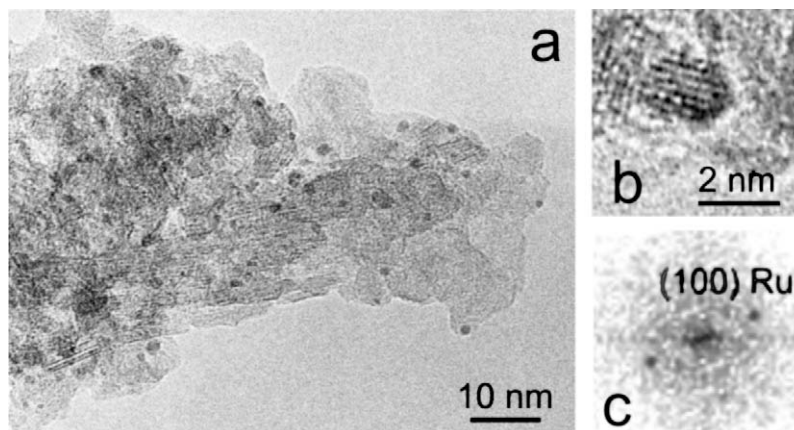


Fig. 1. (a) Representative TEM image of the as-prepared 1.1% Ru/ γ -Al₂O₃ catalyst, (b) HRTEM image of individual Ru nanoparticle and (c) the FFT pattern from the crystalline particle corresponding to 0.234 nm lattice fringes [Ru(1 0 0)].

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