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Sintering of Colloidal Ru/γ-Al_2O_3 Catalyst in Hydrogen

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Abstract Colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst was prepared by a microwave assisted, solvothermal reduction of $RuCl_3$ in ethylene glycol in the presence of γ-Al_2O_3. The catalyst subjected to heat-treatment in hydrogen up to 700 °C, was characterized by BET, XRD, TEM and H_2 chemisorption. As-prepared catalyst contained Ru nanoparticles with mean size of 1.5 nm and narrow size distribution uniformly distributed over the support. The nanoparticles were stable on the alumina to 500 °C, but treatment at 600–700 °C caused some sintering of Ru due to migration and coalescence of a part of smallest ruthenium nanoparticles. However, even after H_2 treatment at 700 °C, large amount of Ru nanoparticles with sizes of 1–3 nm remained in the catalyst. H_2 chemisorption data revealed decrease of Ru dispersion from 0.28 to 0.19 by hydrogen treatment at 700 °C and were in good correspondence with TEM results. On the contrary, mean crystallite sizes obtained from XRD were strongly overestimated.

Keywords Ru nanoparticles · Thermal stability · XRD · TEM · Hydrogen chemisorption

1 Introduction

Ruthenium nanocatalysts have been proven to be exceptionally active and selective for few industrially relevant chemical reactions including ammonia synthesis/decomposition [1–4], the partial oxidation of methane [5–7] and partial hydrogenation of benzene [8]. The ammonia synthesis/decomposition and partial oxidation of methane are structure sensitive reactions, hence the catalytic activity and selectivity are strongly related to the morphology of the supported metal particles (size and shape). We reported recently that well-defined ruthenium nanoparticles can be obtained by the colloid method and then deposited on the alumina support [9]. Miyazaki et al. [3], and Balint et al. [7, 10, 11] also prepared the Ru/Al_2O_3 catalysts by deposition Ru nanoparticles obtained by reduction of $RuCl_3$ precursor onto an alumina support. High resolution transmission electron microscopy (HRTEM) studies showed that the colloidal Ru/Al_2O_3 catalysts have smaller mean metal particle size and narrower particle size distribution than traditional catalysts prepared by wet impregnation from the same $RuCl_3$ precursor [9, 12].

The stability of metal nanoparticles deposited on oxide support is a fundamental issue in catalysis studies. For example, high temperature treatment can cause morphological changes of the dispersed metal particles due to sintering and/or metal–support interactions. Till now such studies have been done on traditionally prepared ruthenium catalysts [13–15]. Narita et al. [13] found by XRD that Ru particle size in Ru/SiO_2 catalyst was almost constant for the reduction temperature below 630 °C but it increased significantly at 730 °C. Similarly, some sintering of the Ru particles was observed in the Ru/Al_2O_3 system at reduction temperatures above 630 °C [14] or in the Ru/MgO catalyst at/or above 700 °C [15, 16]. However, systematic study of

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morphology changes of Ru in conventional catalysts is difficult due to a broad distribution of metal particle sizes and non-uniform distribution of particles on the support [15].

In this work we investigated for the first time the stability of colloidal ruthenium nanoparticles supported on alumina during thermal treatment in hydrogen. Such studies are important because in the catalyst prepared by the colloidal method, Ru particles are much weaker bond with the support than the particles in the catalysts prepared by conventional impregnation method [3]. Colloidal Ru nanoparticles were prepared by a novel, microwave assisted polyol reduction method in the presence of alumina support. Thanks to much shorter heating time than that used in traditional conductive heating, such as an oil bath used by Balint et al. [7, 10, 11], smaller, more uniform Ru nanoparticles were obtained. Structure of the catalysts was characterized by BET, XRD, TEM, HRTEM and SAED. The dispersion of Ru in the colloidal catalyst was determined by H_2 chemisorption method.

2 Experimental

2.1 Catalyst Preparation

The colloidal catalyst was prepared by the solvothermal reduction of $RuCl_3 \cdot 3H_2O$ with ethylene glycol in the presence of γ-alumina [9]. First, an appropriate amount of the ruthenium precursor was dissolved in ethylene glycol and then γ-Al_2O_3 was added to form a suspension. The reduction was carried out at 180 °C for 10 min, in a microwave accelerated reaction system (MW Reactor Model 02-02 ERTEC, Poland). After this time, the mixture was rapidly cooled down in an ice-water bath. The suspension was diluted with an aqueous solution of $NaNO_3$ to remove organic solvent. The solid product was filtered off, washed several times with distilled water and dried under vacuum at room temperature. Such as-prepared catalyst was thoroughly characterized and then was heated in a quartz tube in hydrogen flow at 500, 600 and 700 °C for 5 h.

2.2 Catalyst Characterization

The as-prepared catalyst contained 5.1 ± 0.1 wt% Ru (as determined by the ICP-AES method) and according to XPS and chemical analysis was free of chlorine contamination [9]. The total surface area was determined by using the standard BET method with the samples being degassed for 3 h at 250 °C.

The morphology and structure of the catalyst samples after each stage of thermal treatment were studied with Philips CM20 Super Twin microscope (TEM) at an acceleration voltage of 200 kV. The specimens were prepared by placing a droplet of ultrasonic dispersed suspension of the sample in methanol on a standard copper grid covered with carbon and allowing the solvent to evaporate. The crystal structure was determined by analysis of selected area diffraction (SAED) patterns and was complemented by analysis of high-resolution electron microscopy (HRTEM) micrographs. The size distribution and mean size of Ru nanoparticles were determined on the basis of size measurements of 400–500 particles for each sample. The measurements were done manually using the ImageJ program [17]. The structure of the samples was also examined using powder X-ray diffraction (XRD) with the use of the DRON-3 diffractometer (Ni-filtered CuK_α radiation). The mean crystallite size of Ru was calculated using the Scherrer equation.

The specific active metal surface area was determined by hydrogen chemisorption using a conventional volumetric apparatus [9]. Prior to the H_2 chemisorption, the catalyst sample was in-situ pre-treated with H_2 (200 Torr) at 400 °C for 2 h. It was then outgassed to $\sim 10^{-6}$ Torr for 2 h at the same temperature and cooled under vacuum to the adsorption temperature. Isotherms of total and reversible hydrogen adsorption at 100 °C on all samples were determined using an equilibration time of 2 h for the first dose of hydrogen and 1 h for the subsequent doses.

3 Results and Discussion

3.1 Hydrogen Chemisorption

Figure 1 presents the total and reversible isotherms of hydrogen chemisorption at 100 °C for the as-prepared

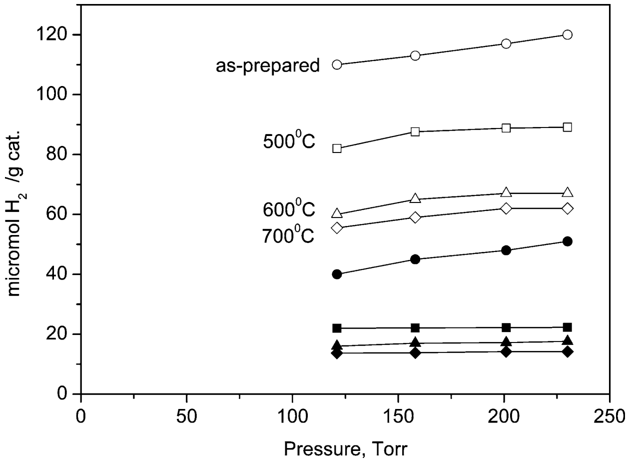

Fig. 1 Isotherms for H_2 chemisorption on as-prepared colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst (○, ●), and after treatment in H_2 at 500 °C (□, ■), 600 °C (Δ, ▲) and 700 °C (◇, ◆). Open and closed symbols represent the respective total and reversible gas uptakes at 100 °C

colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst and the catalyst after treatment in hydrogen at 500–700 °C. The total and reversible hydrogen isotherms show a linear dependence with pressure in the 120–230 Torr range. It is evident, that the total and reversible hydrogen uptakes show maximum for the as-prepared colloidal catalyst and then the uptakes decreased slowly with rise of the temperature treatment of the catalyst. The results of the volumetric chemisorption on all samples are summarized in Table 1. It is interesting to note, that the fraction of reversibly chemisorbed hydrogen (30 μmol/g cat.) represents as much as 30% of the total chemisorption (100 μmol/g cat.) for the as-prepared catalyst and drops to about 22% for the catalyst treated at 700 °C. In this study, reversibly adsorbed hydrogen is defined as that which can be removed from the catalyst by a 10 min evacuation at 10^{-6} Torr at 100°C. The nature of adsorbed hydrogen on Ru, especially of the weakly adsorbed one, is still under discussion. Literature data show that hydrogen reversibly adsorbed on the ruthenium metal phase may exist in either a precursor state or a state of low adsorption energy [16, 18–21]. It was proposed that such weakly bound hydrogen is initially adsorbed at low-coordination sites (edge and corner) and it is highly mobile [16, 18, 19]. Similar mechanism of hydrogen adsorption and dissociation has been shown to be efficient at low-coordination sites on the platinum metal [22]. Sayari et al. [20] found that at room temperature reversible H_2 chemisorption occurs in appreciable amounts on the Ru crystallites with sizes within the limited range of 0.9–2.2 nm. Also, Yang and Goodwin [21] reported that the fraction of reversible H_2 chemisorption on dispersed Ru is a function of an average particle size. Zupanc et al. [16] explained this finding by a modification in the surface energetics of the Ru crystallites with the change of their size. The authors found, that during adsorption on Ru/MgO catalyst H_2 dissociates preferentially on the low-coordinated defect-like sites, producing the very weakly bound hydrogen species. Next, these species migrate to sites that adsorb hydrogen more strongly. Moreover, the thermal treatment in hydrogen from 510 to 1,050 °C cause a loss of defect-like sites and the total amount of active sites for H_2 adsorption diminished by about 50% [16]. Our chemisorption results show that the ratio of the reversibly to irreversibly adsorbed hydrogen decreased from 0.43 in the as-prepared Ru/γ-Al_2O_3 catalyst to 0.27 after treatment under H_2 up to 700 °C. It is likely that the as-prepared Ru/γ-Al_2O_3 catalyst, obtained by the colloid route, contained rather large amount of the low-coordinated defect-like sites which decreased upon heating treatment. The difference between the total and the reversible adsorption yields the amount of strongly chemisorbed hydrogen, which after extrapolation to zero pressure, gives the capacity of a hydrogen monolayer. As shown in Table 1, the irreversible H_2 uptakes also decreased gradually on raising the treatment temperature.

Ruthenium dispersion (H/Ru) and the specific metal surface area were determined from irreversible H_2 uptakes, assuming the chemisorption stoichiometry H_{irr}:$Ru_s = 1$:1 [9, 23] and the surface area occupied by one Ru atom of 8.17 $Å^2$ [20, 21]. Calculation of a metal dispersion from the amount of the strongly bound hydrogen was proposed by Goodwin's [20, 21, 23] and King's [18, 19] groups and was used also in our previous studies [9]. As can be seen, the dispersion and the ruthenium surface area decreased by about 32% after hydrogen treatment of the as-prepared catalyst at 700 °C (Table 1). The loss of the active surface area is usually connected with the growth of small metal particles to more stable, large ones. The H_2 chemisorption results indicate that rather moderate metal sintering of the colloidal Ru catalyst is induced by the heat treatment in hydrogen up to 700 °C. BET data included in Table 1, show that deposition of Ru nanoparticles from colloidal solution did not change the surface area of γ-Al_2O_3. However, the alumina support underwent slight textural changes upon hydrogen treatments up to 700 °C, with some loss of the surface area, which may be responsible also for decrease in the active surface of ruthenium due to pore closure.

3.2 Structure Characterization by XRD and TEM

Figure 2 depicts XRD patterns of the colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst subjected to heat treatment in hydrogen. The pattern of the as-prepared catalyst contains only

Table 1 BET surface area and hydrogen chemisorption on colloidal 5.1% Ru/γ-Al_2O_3 catalyst

Catalyst treatment	S_{BET}[a] (m^2/g)	H_2 uptake (μmol/g cat.)			Dispersion[b] (H/Ru)	Specific metal surface area (m^2/g cat.)
		Total	Reversible	Irreversible		
As-prepared	249	100	30	70	0.28	6.89
H_2, 500 °C	241	89	23	66	0.26	6.49
H_2, 600 °C	213	67	17	50	0.20	4.92
H_2, 700 °C	195	62	14	48	0.19	4.72

[a] BET surface area of pure alumina support was 245.9 m^2/g

[b] Dispersion of Ru—number of irreversibly chemisorbed hydrogen atoms to the total number of Ru atoms

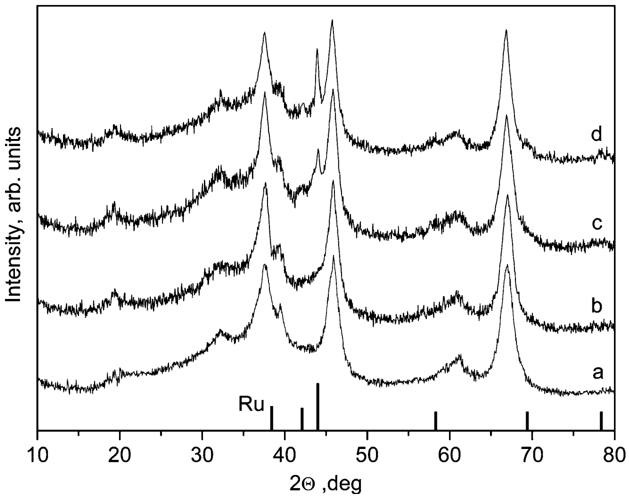

Fig. 2 XRD patterns of colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst. **a** as-prepared, **b** heated in H_2 at 500 °C, **c** 600 °C, **d** 700 °C. Schematic diffraction pattern of Ru standard is also shown

Table 2 The mean size of Ru particles in colloidal Ru/γ-Al_2O_3 catalyst measured by various methods

Catalyst treatment as-prepared	Mean size from irreversible H_2 uptake (nm)	*d*(TEM) (nm)	*d*(XRD) (nm)
	2.9	1.5	Ru not visible
H_2, 500 °C	3.2	2.4	Ru not visible
H_2, 600 °C	4.3	2.8	6.4
H_2, 700 °C	4.4	3.2	12.8

reflections of γ-Al_2O_3 (JCPD File Nr. 10-0425). After treatment at 500 °C very weak bump occured at 2θ–44°, where the strongest (101) reflection of Ru is expected. With rising a heat treatment temperature to 600 and 700 °C intensity of Ru (101) reflection significantly increased, and its width decreased, indicating crystallite growth. However, no measurable change of the γ-Al_2O_3 reflections was noticed. Mean crystallite sizes of Ru calculated from XRD data are given in Table 2.

TEM images of the catalyst samples are presented in Fig. 3. As can be seen, the as-prepared catalyst (Fig. 3a) contains very small metal particles uniformly dispersed over the support. Analysis of HRTEM images revealed, that the particles are crystalline and observed lattice fringes fit those of Ru (inset to Fig. 3a). The particles have very narrow size distribution (97% of the particles have sizes between 1 and 2.5 nm) and the mean size of 1.5 nm. Recently, Bedford et al. [24] showed, by using high-energy X-ray diffraction, that Ru particles that are only 2 nm in size are heavily disordered. Heating at 500 °C caused some broadening of the particle size distribution (Fig. 4b) and increase of the mean particle size to 2.4 nm. The particles have better developed crystal faces with no evidence of any amorphous surface layer (inset to Fig. 3b). At higher temperatures, 600 and 700 °C, significant broadening of the particle size distribution occurred with formation of a fraction of bigger particles much exceeding the mean size. These bigger particles produced spot reflections visible in SAED patterns (insets to Fig. 3c, d).

As was shown in the previous section the reversible H_2 chemisorption represents only a fraction (30%) of the total hydrogen held by the as-prepared catalyst. Taking into account very narrow distribution of the particle sizes in this sample (c.f. Fig. 4a) we cannot easily assign different kinds of adsorption (reversible or irreversible) to particular fraction of Ru particles. Evidently each individual particle participates in both. The fact that after heat treatment at high temperatures contribution of the reversible adsorption decreases correlates well with observed change in the particle size distribution. There is a decrease in the fraction of the smallest, irregular particles but instead larger, well developed particles occur (Fig. 3). The latter particles exhibit mostly dense (0 0 1) or (1 0 0) faces with low number of low-coordinated sites.

Table 2 summarizes the mean particle sizes calculated from hydrogen chemisorption (irreversible uptake), TEM and XRD techniques. The mean particle sizes were calculated from the hydrogen chemisorption using the relation $d(\text{chem}) = 5/S \cdot \rho$, where S is the metal specific surface area and ρ is the density of ruthenium [9]. The TEM, XRD and hydrogen chemisorption data showed increase of the mean size of Ru particles with thermal treatment of the colloidal Ru catalyst. For the as-prepared 5.1 wt% Ru/γ-Al_2O_3 catalyst TEM as well as BET results indicate that the ruthenium particles are located mostly at the surface of the alumina grains, though some of them also inside the pores. The later particles posses strongly restricted ability of translational movement. TEM data confirms this view because heating in H_2 already at 500 °C caused some agglomeration of the small Ru particles. However, only very small change in the mean size of Ru particles was detected by the hydrogen chemisorption. More severe particle agglomeration was observed after heating at higher temperatures, especially at 700 °C. It should be mentioned however, that there are important discrepancies between mean particle sizes calculated using various methods. Though the results from H_2 chemisorption and TEM converge, the XRD data are evidently too high. TEM data (Figs. 3, 4) show clearly that the reason is the presence of a large population of very small Ru particles in the samples heated at 600 and 700 °C. About 60% and 50% of the particles have still sizes between 1 and 2.5 nm, respectively and these particles were overlooked by the XRD method. It means that this fraction of the metal particles is

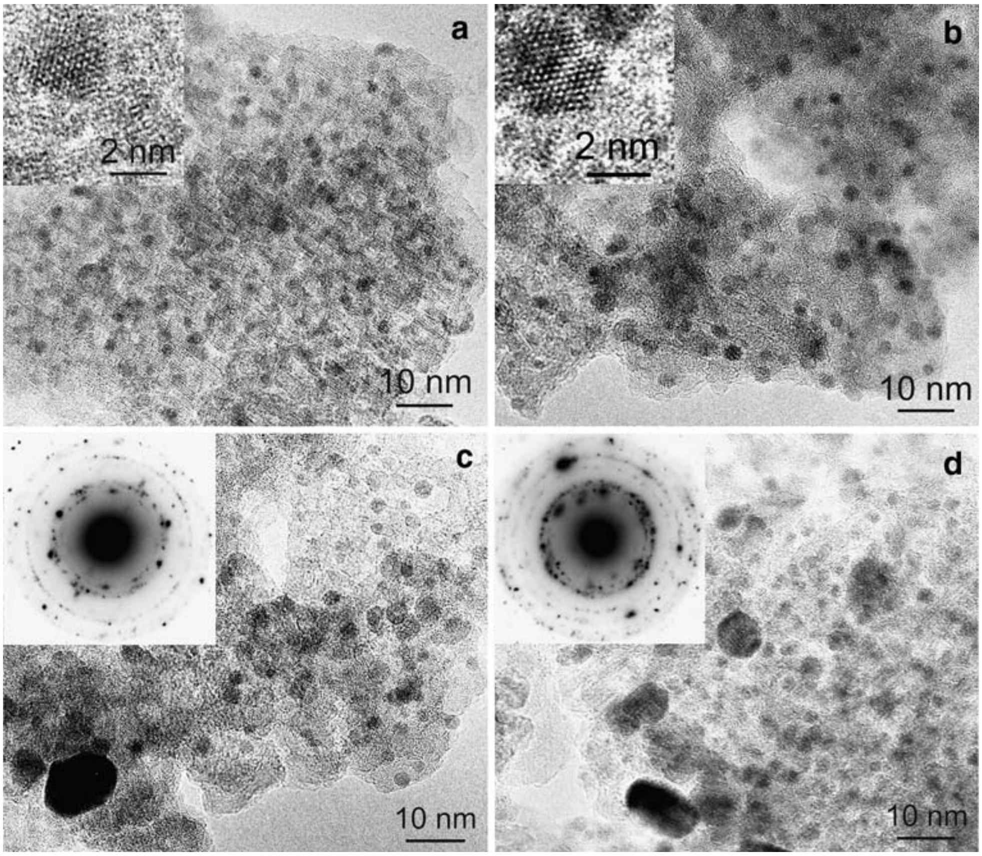

Fig. 3 TEM images of colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst: **a** as-prepared, **b** heated in H_2 at 500 °C, **c** 600 °C, **d** 700 °C. HRTEM images of individual Ru particles (insets to **a** and **b**) and SAED patterns (insets to **c** and **d**) are also shown

resistant to sintering. Some decrease in the fraction of the smallest particles after heating in H_2 at 500 °C observed by TEM, as well as the asymmetrical broadening of the particle size distributions towards larger sizes (Fig. 4) indicate that the particle growth occurs via a migration–coalescence mechanism [25]. In general, such sintering mechanism of the metal phase is favored in the systems that show a weak metal–support interaction. In our colloidal Ru/γ-Al_2O_3 catalyst prepared by a microwave-polyol method Ru adsorbs at the γ-alumina rather as neutral particles than as ions. As a result, the ruthenium particles are not attached strongly to the alumina support.

Summarizing, the results presented in this study suggest that the colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst prepared by a microwave assisted, solvothermal reduction of $RuCl_3$ in ethylene glycol in the presence of γ-Al_2O_3 contains two fractions of Ru nanoparticles. Ru nanoparticles of the first fraction, located at the outer surface of the support, have a tendency to agglomerate. The particles of the second fraction, deposited in the alumina pores, have strongly limited space for movement and growth. It can be noted, that γ-alumina used in this study is highly porous, with surface area of 245.9 m^2/g, pore volume of 0.21 cm^3/g and the pore diameter of 1–5 nm. Nevertheless, the presence of narrow and intense Ru reflections in the XRD patterns of the catalysts heated at 600 and 700 °C, as well as the presence of large particles in TEM images, indicate that a significant amount of the precious metal has been lost as catalytically active phase. It means, that possible application of the colloidal Ru/γ-Al_2O_3 catalysts would be limited to the mild reaction conditions, i.e., temperatures nor exceeding 500 °C. Very recently, Galletti et al. [26] used successfully the colloidal Ru/γ-Al_2O_3 catalysts for hydrogenation of phenol to cyclohexanone at 160 °C in slurry phase. However, in line with our data, some authors have reported undesirable ruthenium colloid aggregation during catalytic reactions carried out at temperatures 350–650 °C [27] or at 400–600 °C [10, 11]. In near future, the colloidal Ru/γ-Al_2O_3 catalysts will be tested in our laboratory in structural-insensitive reactions like gas-phase hydrogenation of benzene.

4 Conclusions

Thermal stability of Ru nanoparticles supported on γ-Al_2O_3 was examined in reducing conditions, at temperatures up to 700 °C. The results show that Ru

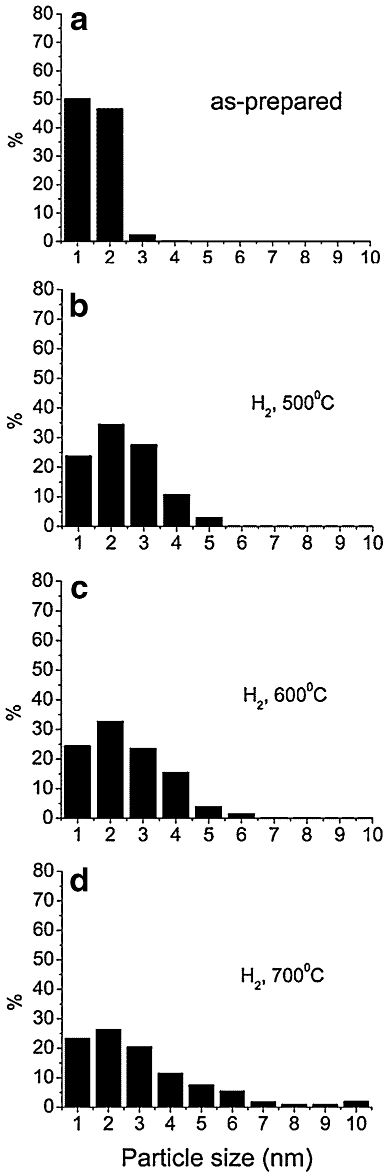

Fig. 4 Size distributions of Ru particles in colloidal 5.1 wt% Ru/γ-Al_2O_3 catalyst: **a** as-prepared, **b** heated in H_2 at 500 °C, **c** 600 °C, **d** 700 °C

nanoparticles are stable at the surface of the alumina support up to 500 °C, but heating in H_2 at 600–700 °C induces a migration and coalescence of certain part of the smallest ruthenium nanoparticles. However, even after treatment at 700 °C, large amount of small Ru particles, with sizes similar as in the as-prepared colloidal catalyst, remained at the surface.

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References

1. Zhang J, Xu H, Ge Q, Li W (2006) Catal Commun 7:148
2. Seetharamulu P, Kumar VS, Padmasri AH, Raju BD, Rao KSR (2007) J Mol Catal A 263:253
3. Miyazaki A, Balint I, Aika K, Nakano Y (2001) J Catal 204:364
4. Xu Q-Ch, Lin J-D, Li J, Fu X-Z, Liang Y, Liao D-W (2007) Catal Commun 8:1881
5. Perkas N, Zhong ZY, Chen LW, Besson M, Gedanken A (2005) Catal Lett 103:9
6. Li HL, Wang RH, Hong Q, Chen LW, Zhong ZY, Koltypin Y, Calderon-Moreno J, Gedanken A (2004) Langmuir 20:8352
7. Balint I, Miyazaki A, Aika K (2003) J Catal 220:74
8. Ning JB, Xu J, Liu J, Lu F (2006) Catal Lett 109:175
9. Okal J, Zawadzki M, Kępiński L, Krajczyk L, Tylus W (2007) Appl Catal A Gen 319:202
10. Balint I, Miyazaki A, Aika K (2002) J Catal 207:66
11. Balint I, Miyazaki A, Aika K (2002) Chem Commun 6:630
12. Lafaye G, Siani A, Marecot P, Amiridis MD, Williams CT (2006) J Phys Chem B 110:7725
13. Narita T, Miura H, Sugiyama K, Matsuda T, Gonzalez RD (1987) J Catal 103:492
14. Narita T, Miura H, Ohira M, Hondou H, Sugiyama K, Matsuda T, Gonzalez RD (1987) Appl Catal 32:185
15. Murata S, Aika K (1992) Appl Catal A 82:1
16. Zupanc C, Hornung A, Hinrichsen O, Muhler M (2002) J Catal 209:501
17. Rasband W, ImageJ, U.S. National Institutes of Health, Bethesda, Maryland, USA, http://rsb.info.nih.gov/ij/, 1997–2005
18. Uner DO, Pruski M, King TS (1995) J Catal 156:60
19. Vander Wiel DP, Pruski M, King TS (1999) J Catal 188:186
20. Sayari A, Wang HT, Goodwin JG Jr (1985) J Catal 93:368
21. Yang CH, Goodwin JG Jr (1982) J Catal 78:182
22. Bernasek SI, Somorjai GA (1975) J Chem Phys 62:3149
23. Goodwin JG Jr (1981) J Catal 68:227
24. Bedford N, Dablemont C, Viau G, Chupas P, Petkov V (2007) J Phys Chem C 111:18214
25. Datye AK, Xu Q, Kharas KC, McCarty JM (2006) Catal Today 111:59
26. Galletti AMR, Antonetti C, Longo I, Capannelli G, Venezia AM (2008) Appl Catal A Gen doi:10.1016/j.apcata.2008.07.044
27. Balint I, Miyazaki A, Aika K (2003) React Kinet Catal Lett 80:81