Ru nanoparticles stabilized by organosilane fragments: Influence of the initial Si/Ru ratio and thermal stability

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Abstract. The decomposition of the organometallic ruthenium precursor [Ru(COD)(COT)] (COD: 1,5-cyclooctadiene; COT: 1,3,5-cyclooctatriene) in mild conditions (20 °C, 3 bar H_2) in n-pentane leads, in the presence of octylsilane ($H_3SiC_8H_{17}$) to the formation of stable Ru nanoparticles with narrow size distribution. The solids obtained after washing and drying were fully characterized by elemental analysis, TEM with EDX, infra red measurements as well as solid state ^{13}C CP-MAS NMR investigations. The influence of the initial octylsilane/Ru(COD)(COT) ratio ranging from 0.2 to 2.0 was studied. It was observed that the size of the nanoparticles decreases with the initial Si/Ru ratio. The thermal stability of these nanoparticles (Si/Ru = 1) was also studied and as expected the size of the particles drastically increases after treatment under H_2 at 500 °C, while surprisingly under neutral atmosphere, there is only a slight increase.

PACS. 61.46.Df Nanoparticles

1 Introduction

Nanoparticles of various metals e.g. Au, Pd, Pt, Ru... with diameters in the nanometer range are currently prepared, using various organic compounds as stabilizers [1–11]. As example, ruthenium nanoparticles of about 2 nm were prepared by the decomposition of Ru(COD)(COT) (COD: 1,5-cyclooctadiene, COT: 1,3,5-cyclooctatriene) in mild conditions (20 °C, 3 bar H_2) and in presence of amines, alcohols or thiols as stabilizers [12,13]. To our knowledge, these particles are not stable under treatment at high temperature since heat treatment leads to drastic sintering of the particles [14].

We recently demonstrated that Ru nanoparticles of about 2.4 nm in diameter, covered by octylsilane fragments can be prepared [15] by the Surface Organo-Metallic Chemistry on Metals route [16], using Ru(COD)(COT) as precursor and octylsilane (H_3Si-C8) as stabilizer. In our case, the presence of grafted ≡Si-C8 fragments on the surface of the particles was evidenced by IR spectroscopy and solid state ^{13}C CP-MAS NMR. This is different from the organosilane functionalized gold nanocrystal prepared by Fan et al. [17] where the silane function is in the external layer of the micelle. The created Ru-Si bond is very strong and can present advantages forming a stable catalyst with a defined hydrophobic layer (alkyl chain) in order to organize the substrates in a selective way.

2 Results and discussion

Using the procedure already described [15] and starting with a H_3Si-C8/Ru(COD)(COT) initial ratio varying from 0.2 to 2.0, Ru particles with diameter (d) varying from 1.6 to 3.2 nm were obtained (Tab. 1). The dispersion of the particles ($D = Ru_s/Ru$, where Ru_s and Ru are the number of surface ruthenium atoms and the total number of atoms) were calculated assuming a cuboctahedral shape. It must be point out that the results of both elemental analyses (which correspond to macroscopic values) and EDX (which gives the amount of each element on a given particle or on a small number of particles) are comparable, showing that the samples are highly homogeneous. An average stoichiometry vs. total ruthenium atoms of the particles $Ru[Si(n\text{-}C_8)_x]_y$ can be given using the results of elemental analysis. The silicon to total ruthenium ratio of the particles indicates that up to an initial Si/Ru ratio of ca. 0.6 all silicon has been "chemisorbed" on the particles. Increasing the amount of octylsilane does not result in the incorporation of a higher amount of silicon, leading to the conclusion that for initial Si/Ru ratio greater than ca. 0.6, the excess of silane which was not grafted is removed by washing.

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Table 1. Particles sizes and dispersions deduced from TEM data and results of elemental analysis (E.A.) and EDX measurements for Ru/Si-C$_8$ particles.

Initial Si/Ru ratio	0.2	0.5	1.0	2.0
d^a (nm)	1.6	1.6	2.3	$\sim$3
D^b (Ru$_s$/Ru)	0.61	0.59	0.48	n.d.
Ru (% w) E.A.^{c}	69.5	70.0	68.4–68.6	70.9
Ru (% w) EDX	69.0	71.0	69.0	83.0
Si (% w) E.A.	5.3	11.2	9.2–10.4	14.3
Si (% w) EDX.	5.2	11.0	11.0	14.0
C (% w) E.A.	4.1	11.5	19.5–24.4	32.8
Si/Ru (average)	0.28	0.57	0.54	0.67
x = C8/Si (E.A.)	0.22	0.30	0.62–0.68	0.67
Stoichiometry vs. Ru	Ru[Si(C8)$_{0.22}$]$_{0.28}$	Ru[Si(C8)$_{0.30}$]$_{0.57}$	Ru[Si(C8)$_{0.65}$]$_{0.54}$	Ru[Si(C8)$_{0.67}$]$_{0.67}$
Si/Ru$_s$	0.46	0.97	1.13	–

^{a} Scanning transmission electron microscopy with EDX was carried out at the Institut de Recherches sur la Catalyse, CNRS, Villeurbanne, France, using JEOL 100 CX electron microscope. The mean particle diameter (d) was determined by observation of more than 200 particles from 5 TEM pictures.
^{b} Dispersion (D) of the sample is the ratio between number of surface Ru atoms Ru$_s$ and the total number of atoms in a particle of a diameter (d).
^{c} Elemental analyses were performed at the Laboratoire de Synthèse et Électrosynthèse Organométalliques, UMR 5188 CNRS, Dijon, France for carbon and hydrogen and at the Service Central d'Analyse, Département Analyse Élémentaire, CNRS, Vernaison, France for ruthenium and silicium. All sample preparations were realized under argon and the elemental analyses were done without contact with air.
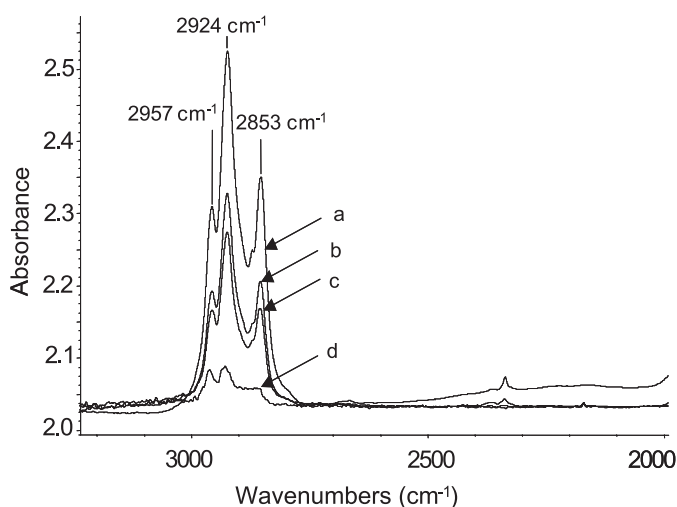
Fig. 1. Infra red spectra of Ru/Si-C8 particles stabilized with (a) 2.0, (b) 1.0, (c) 0.5 and (d) 0.2 eq. of octylsilane.

Infrared spectroscopy of the dried solids, embedded in KBr, following the procedure already described [15] are represented in Figure 1.

These spectra demonstrate that Si-H vibrations, expected at 2100 cm^{-1} are totally absent whatever the initial Si/Ru ratio. We can then conclude that all silicon hydrides had reacted during the grafting reaction of the silane on the metal particle, in complete accordance with Hostetler et al. [18] who found that primary organosilanes react readily with transition metal surfaces at temperature below –20 °C with formation of surface-bound silylines. Since $\nu$(CH$_2$) and ν(CH$_3$) vibrations are still observed in the 2800–3000 cm^{-1} region, the presence of $\equiv$Si-C8 fragments on the surface is then evidenced, as demonstrated in the previous work [15].

Solid state NMR data are in agreement with this conclusion. If one excepts the sample with the lowest silane content, for which the signal to noise ratio is very bad (due to the low amount of carbon), all spectra show four well-resolved peaks at 32.9, 29.7, 23.1 and 14.4 ppm. The signal at 14.4 ppm can be attributed to the terminal methyl group of the octyl ligand, those at 27.3 and 29.7 ppm to the C$_\beta$ and C$_\gamma$ carbon atoms and that at 32.9 to the methylene groups of the chain. Only the C$_\alpha$ signal, expected at 6.2 ppm is missing due to the proximity to the metal surface in accordance with the literature [12].

From these results, we can expect at the surface of the ruthenium particles the presence of only two species, naked silicon atoms that is silicon for which the Si–carbon chain has been cleaved and $\equiv$Si-C8 fragments. Assuming that all silicon atoms are located on the surface of the ruthenium particles, the value corresponding to Si/Ru$_s$ can be given, almost for starting Si/Ru ratio of 0.2; 0.5 and 1.0 (Tab. 1). It seems that the Si/Ru$_s$ value increases with the initial Si/Ru, up to a maximum of about one, which corresponds to a full coverage of the metallic surface. As seen in Table 1, the x value (C8/Si) increases with the y (Si/Ru$_s$) value. This means that the hydrogenolysis of the Si-C8 bond is deeper at low coverage of the ruthenium surface by Si. This result is in perfect agreement with previous results obtained by reaction of tetrabutyl tin (Sn(n-C$_4$H$_9$)$_4$) on Rh/SiO$_2$ or Pt/SiO$_2$ catalysts [19,20] and could be interpreted by a "poisoning" effect of the Si grafted on the metallic surface toward hydrogenolysis of the Si-C8 bond.
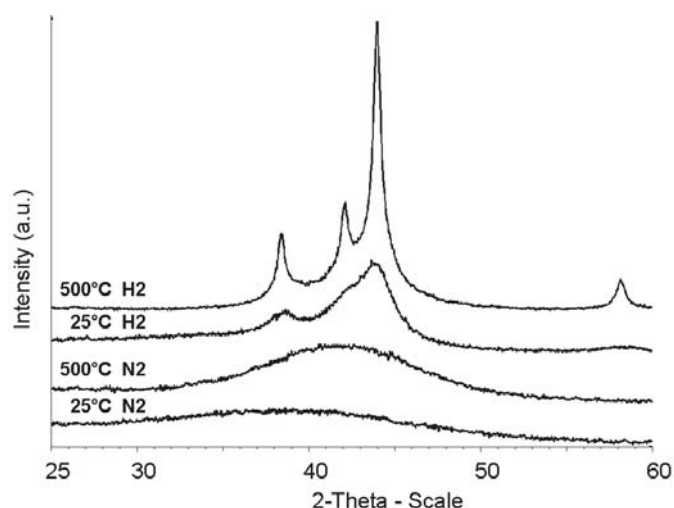
Fig. 2. XRD pattern of Ru particles after heat treatment under N_2 or H_2 at 25 °C or 500 °C.
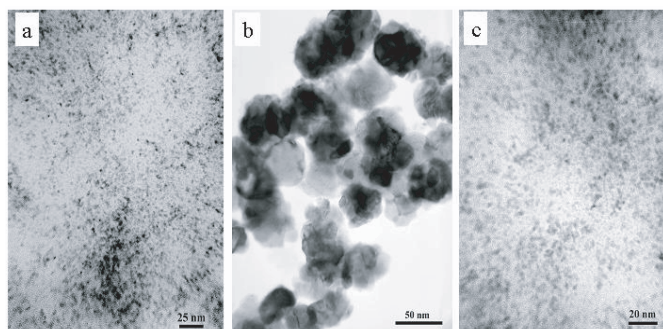
Fig. 3. TEM images of Ru particles, initial material (a), treated at 500 °C under flowing H_2 (b) or N_2 (c).

These particles (starting with Si/Ru = 1) were treated, under flowing H_2 or N_2, in a reaction chamber designed for in situ XRD analysis. The temperature program for both cases was the following: increasing of the temperature from room temperature to 500 °C with 0.5 °C/min, then 3 hours at 500 °C. The XRD patterns of the sample treated at 25 °C under N_2 (Fig. 2) show only a broad band of very small intensity, which is compatible with very small Ru particles, in accordance with TEM analysis (Fig. 3). After treatment under flowing H_2 up to 500 °C, relatively sharp peaks corresponding to the Ru crystallographic structure were observed, showing the sintering of the particles. Even at 25 °C under H_2 one can already observe a small increase in size compared to the original sample. In the contrary, treatment under flowing N_2 leads to a very small change in the XRD pattern, evidencing a small evolution of the size of the Ru nanoparticles. This unexpected result was confirmed by TEM analysis of the samples after treatment. As shown in Figure 3, very large Ru particles of about 50 nm are obtained after treatment in H_2 while almost unchanged particles were observed after treatment under neutral atmosphere.

It is obvious that under flowing H_2, a drastic sintering of the particles occurs although under N_2, a protecting layer is formed on the metallic surface which inhibits the coalescence of the particles, even at temperature as high as 500 °C.

3 Conclusions

In conclusion, it has been demonstrated that small ruthenium nanoparticles with average diameter ranging from 1.6 to 2.3 nm can be obtained using various octylsilane/Ru(COD)(COT) ratios (0.2, 0.5, 1.0 and 2.0). These small metallic particles were characterized by elemental analysis, TEM, IR and solid state ^{13}C MAS NMR. It was observed that the smallest particles were obtained for the lowest Si/Ru ratio (0.2). Two species exist on the surface of the particles, naked silicon atoms and ≡Si-C8 fragments. Naked silicon atoms are predominant for initial Si/Ru ratio of 0.2 and 0.5, while for higher coverage the ≡Si-C8 fragments are majority. These nanoparticles exhibit unexpected stability toward heat treatment under neutral atmosphere. Under these conditions, a protecting layer is formed on the metallic surface which inhibits the coalescence of the particles, even at temperature as high as 500 °C as shown by in situ XRD measurements.

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