



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

K. Pelzer^{1,*}, J.P. Candy², G. Bergeret³, J.M. Basset²

¹Department of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany

²LCOMS, UMR CNRS-CPE 9986, 43 boulevard du 11 novembre 1918, 69616 Villeurbanne, France

³I.R.C., 2 avenue A. Einstein, 69626 Villeurbanne, France

* Corresponding author: e-mail pelzer@fhi-berlin.mpg.de,

Received 1st August 2006 / Received in final form 4 October 2006 Published online 24 May 2007.

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 H₂) in *n*-pentane leads, in the presence of octylsilane (H₃SiC₈H₁₇) 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 ¹³C 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 H₂ at 500 °C, while surprisingly under neutral atmosphere, there is only a slight increase.

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 H₂) 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 (H₃Si-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 ¹³C 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 H₃Si-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 ($D = R_{\text{us}} / R_{\text{u}}$, where *R_{us}* and *R_u* are the number of surface ruthenium atoms and the total number of atoms) were calculated assuming a cubooctahedral shape. It must be pointed 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*-C₈)*x*]*y* can be given using the results of elemental analysis. The silicon to total ruthenium ratio of the particles

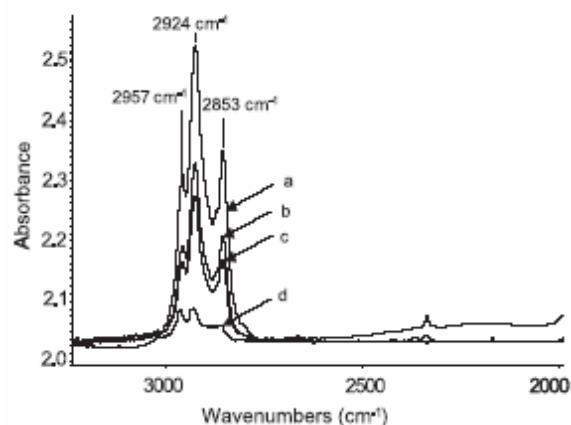
Table 1: Particles sizes and dispersions deduced from TEM data and results of elemental analysis (E.A.) and EDX measurements for Ru/Si-C8 particles.

Initial Si/Ru ratio	0.2	0.5	1.0	2.0
d^a (nm)	1.6	1.6	2.3	~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
$x = \text{C8/Si}$ (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}] _{0.37}	Ru[Si(C8) _{0.68}] _{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 silicon. All sample preparations were realized under argon and the elemental analyses were done without contact with air.

**Figure 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.

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.

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 $-20\text{ }^{\circ}\text{C}$ with formation of surface-bound silylides. Since $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$ vibrations are still observed in the $2800\text{--}3000\text{ cm}^{-1}$ region, the presence of $\equiv\text{Si-C8}$ fragments on the sur-

face is then evidenced, as demonstrate 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 $\equiv\text{Si-C8}$ 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 ($\text{Sn}(n\text{-C}_4\text{H}_9)_4$) on Rh/SiO₂ or Pt/SiO₂ 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.

These particles (starting with Si/Ru = 1) were treated, under flowing H₂ or N₂, 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 $500\text{ }^{\circ}\text{C}$ with $0.5\text{ }^{\circ}\text{C}/\text{min}$, then 3 hours at $500\text{ }^{\circ}\text{C}$. The XRD patterns of the sample treated at $25\text{ }^{\circ}\text{C}$ under N₂ (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

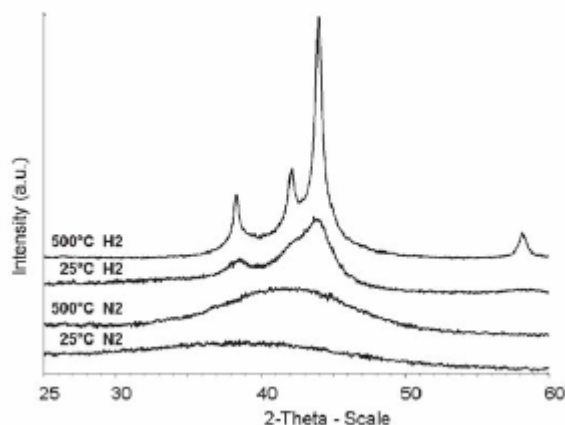


Figure 2: XRD pattern of Ru particles after heat treatment under N₂ or H₂ at 25 °C or 500 °C.

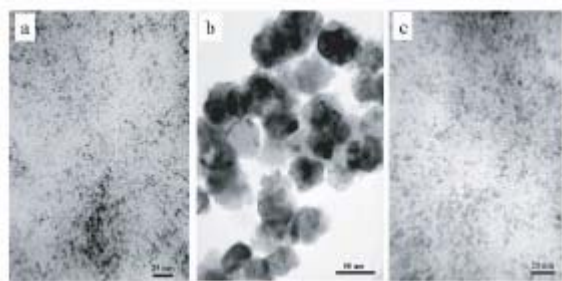


Figure 3: TEM images of Ru particles, initial material (a), treated at 500 °C under flowing H₂ (b) or N₂ (c).

under flowing H₂ 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 H₂ one can already observe a small increase in size compared to the original sample. In the contrary, treatment under flowing N₂ 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 H₂ while almost unchanged particles were observed after treatment under neutral atmosphere.

It is obvious that under flowing H₂, a drastic sintering of the particles occurs although under N₂, 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 ¹³C 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.

Acknowledgement

This work was supported by the DAAD.

References

- H. Bönemann, G. Braun, W. Brijoux, A.S. Tilling, K. Seevogel, K. Siepen, *J. Organomet. Chem.* **520**, 143 (1996)
- H. Bönemann, R.M. Richards, *Eur. J. Inorg. Chem.* **10**, 2455 (2001)
- A.C. Templeton, W.P. Wuelfing, R.W. Murray, *Acc. Chem. Research* **33**, 27 (2000)
- G. Schmid, B. Corain, *Eur. J. Inorg. Chem.* **17**, 3081 (2003)
- M.-C. Daniel, D. Astruc, *Chem. Rev.* **104**, 293 (2004)
- G. Schmid, V. Maihack, F. Lantermann, S. Peschel, *J. Chem. Soc., Dalton Transactions: Inorg. Chem.* **5**, 589 (1996)
- J. Fink, C.J. Kiely, D. Bethell, D.J. Schiffrin, *Chem. Mat.* **10**, 922 (1998)
- F. Dassenoy, K. Philippot, C. Amiens, M.J. Casanove, B. Chaudret, *New J. Chem.* **22**, 703 (1998)
- A. Badia, W. Gao, S. Singh, L. Demers, L. Cuccia, L. Reven, *Langmuir* **12**, 1262 (1996)
- R.H. Terrill, T.A. Postlethwaite, C.-H. Chen, C.-D. Poon, A. Terzis, A. Chen, J.E. Hutchinson, M.R. Clark, G. Wignall, J.D. Londono, R. Superfine, M. Falvo, C.S. Johnson, E.T. Samulski, R.W. Murray, *J. Am. Chem. Soc.* **117**, 12537 (1995)

11. N. Chakroune, G. Viau, S. Ammar, L. Poul, D. Veautier, M.M. Chehimi, C. Mangeney, F. Villain, F. Fiévet, *Langmuir* **21**, 6788 (2005)
12. C. Pan, K. Pelzer, K. Philippot, B. Chaudret, F. Dassenoy, P.M. Lecante, J. Casanove, *J. Am. Chem. Soc.* **123**, 7584 (2001)
13. K. Pelzer, O. Vidoni, K. Philippot, B. Chaudret, V. Collière, *Adv. Funct. Mater.* **13**, 118 (2003)
14. M. José-Yacaman, C. Gutierrez-Wing, M. Miki, D.-Q. Yang, K.N. Piyakis, E. Sacher, *J. Phys. Chem. B* **109**, 9703 (2005)
15. K. Pelzer, B. Laleu, F. Lefebvre, K. Philippot, B. Chaudret, J.P. Candy, J.M. Basset, *Chem. Mat.* **16**, 4937 (2004)
16. J.P. Candy, B. Didillon, E.L. Smith, T.B. Shay, J.M. Basset, *J. Mol. Catal.* **86**, 179 (1994)
17. H. Fan, Z. Chen, C.J. Brinker, J. Clawson, T. Alam, *J. Am. Chem. Soc.* **127**, 13746 (2005)
18. M.J. Hosteler, R.G. Nuzzo, G.S. Girolami, *J. Am. Chem. Soc.* **116**, 11608 (1994)
19. F.Z. Bentahar, F. Bayard, J.P. Candy, J.M. Basset, in *Fundamental and Applied Aspects of Chemically Modified Surfaces*, edited by J.P. Blitz, C.B. Little (The Royal Society of Chemistry 1999), p. 235
20. O.A. Ferretti, C. Lucas, J.P. Candy, J.M. Basset, B. Didillon, F. Le Peltier, *J. Mol. Catal.* **103**, 125 (1995)