

Letter

A versatile one-step method for the preparation of highly dispersed metal supported catalysts

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Abstract

Highly dispersed rhodium particles on various supports have been obtained below 100°C in a single step by using the low pressure organometallic chemical vapour deposition technique in a fluidized bed reactor; these catalysts display a great activity in hydrogenation.

Keywords: Chemical vapour deposition; High dispersions; Metal; Rhodium; Supported catalysts; Vapour deposition

1. Introduction

Preparations of supported metals by reproducible procedures have been known for many years, and are achieved mainly by ion exchange [1] and more recently by using organometallic precursors where the metal is most often in a low oxidation state [2–4]. New modes of preparation of catalysts characterized by small particle sizes have attracted attention very recently [5–15]. At least two steps and generally high temperature reductions are required. For instance, decomposition of fullerene–rhodium composites at 550°C gives rise to small crystallites containing large amounts of rhodium [5]. Preliminary gas phase impregnation of the support followed by a decomposition step above 250°C has been proposed by several authors

[12–15]. Arai et al. [7] have shown that the reduction of platinum precursors which dispersed on alumina with sodium tetrahydroborate at room temperature enhances the catalytic activity compared with catalysts prepared with reductions at 300–400°C.

We have investigated the potential of the low pressure organometallic chemical vapour deposition for the preparation of rhodium supported catalysts from suitable complexes. Three easily handled rhodium compounds, which present vapour pressures ranging from 5 to $8 \cdot 10^{-2}$ Torr (6.7 to 10.8 Pa) at 40–55°C, i.e. $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ **1**, $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ **2** and $[\text{Rh}(\text{acac})(\text{CO})_2]$ **3**, have been selected. Indeed, their thermolysis monitored by infrared and mass spectrometry can be achieved between 80 and 100°C provided the helium carrier gas contains small amounts of dihydrogen. A fluidized bed reactor (Fig. 1) was

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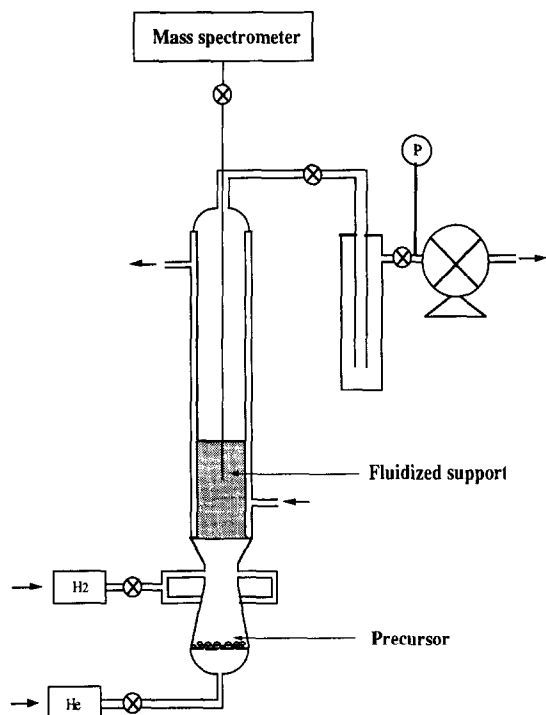


Fig. 1. Schematic diagram of the OMCVD reactor showing the sublimation compartment and the fluidized bed compartment heated by a double jacket. After decomposition the volatile products are condensed in liquid nitrogen trap. P is a pressure gauge.

designed to work under low pressure conditions (50 to 100 Torr) and to prepare the catalyst in a one-step process. Indeed, we observed that immobile support grains lead to inhomogeneous deposits due to the reduced contact between the solid and the precursor vapour.

2. Experimental

The general procedure to prepare a 1% Rh/silica catalyst is as follows. A 0.5 g amount of the rhodium complex was introduced as a powder in the sublimator where glass helices were added to achieve a good carrier gas/solid exchange area. A mass of 6 g of grains of support (silica for instance) was poured into the column.

All the apparatus was placed under reduced pressure (0.1 Torr; 1 Torr = $133.33 \text{ N} \cdot \text{m}^{-2}$) for 1 h during which time the temperature of the bed was maintained at 100°C to remove the water physisorbed on the support, the temperature of the

sublimator was kept at 0°C . Then, the bed was heated to a temperature of 100°C for complex 1, 80°C for complex 2 or 100°C for complex 3 and the pressure in the column was adjusted to 50 Torr by introducing the carrier gas. The sublimator was plunged in a warm bath at a temperature of 53°C for complex 1, 40°C for complex 2 or 55°C for complex 3, and the gas flows (Q_r for the carrier gas and Q_a for the activator gas) were adjusted to 40 and 10 for 1 and 3, 48 and 2 sccm for 2 respectively, a dynamic vacuum being maintained to keep the pressure at 50 Torr. The deposition began for an experiment having a duration of 2.5 h.

At the end of the deposition, the temperature was slowly decreased (1 h) to the room conditions. The vacuum and the gas flows were stopped and a slow air stream (25 sccm) was let into the apparatus until it had reached ambient pressure. The non-sublimated precursor was recovered unchanged. It is noteworthy that the sublimated precursor was deposited in quantitative yield since mass spectrometry measurements showed that no rhodium species are detected beyond the fluidized bed. The catalyst was removed from the column and was used without any further treatment.

3. Results and discussion

The carrier gas (He) is loaded with the vapour of 1, 2 or 3, by letting it flow through the sublimator, then with dihydrogen and the resulting mixture is contacted with the support in the fluidized bed. The temperature of this section has been adjusted so that the decomposition occurs completely and very quickly in the bulk of the fluidized bed.

Representative supports were silica powders that were sieved between 100 and $200 \mu\text{m}$ and that are characterized by a density of 0.23 (group B of the Geldart's classification [16]), and a BET area of $170 \text{ m}^2 \cdot \text{g}^{-1}$; they present a spherical shape as shown by scanning electron microscopy. We observed that a satisfactory compromise between the fluidization of silica and the total pressure of the carrier gas containing the organometallic pre-

Table 1
Characterization of the rhodium deposits

%Rh/SiO ₂	Particle size (nm)	Dispersion	Specific area (m ² ·g ⁻¹)	Porosimetry (cm ³ ·g ⁻¹)
^a	–	–	170	315
0.35 ^b	1.1 ^d	0.97	184	
0.5 ^b	1.2 ^d	0.91	–	
1.0 ^b	1.4 ^d , 1.7 ^e , 1.8 ^f	0.78	178	289
2.0 ^b	1.5 ^d	0.71	172	
1.0 ^c	1.5 ^d	0.71	158 ^g	

^a Pure silica.

^b From [Rh₂(μ-Cl)₂(CO)₄].

^c From [Rh(η³-C₃H₅)₃].

^d By CO chemisorption measurements.

^e Determined by TEM.

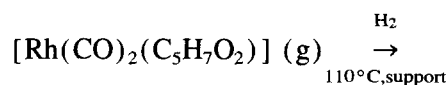
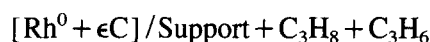
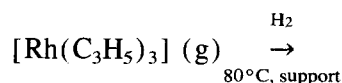
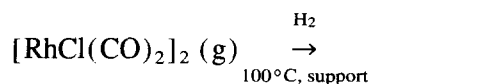
^f From H₂ chemisorption measurements.

^g This silica powder has a specific area of 149 m²·g⁻¹.

cursor was a flow rate of 30–50 sccm for a pressure of 50–100 Torr in a reactor of 30 mm internal diameter. Table 1 displays the main physical characteristics of representative samples. For instance a 1% Rh/SiO₂ (w/w) catalyst, obtained on 6 g of silica for a 5 h deposition, is characterized by a particle size of around 1.5 nm (as determined by three convergent methods, i.e. by H₂ or CO chemisorption measurements and by TEM) and thus a dispersion of 0.78. Moreover, the specific area and the porosity of the support are not affected by the deposition.

As the presence of impurities can have a dramatic influence on the catalytic properties of rhodium supported catalysts, especially in hydrogenation, we focused our attention on the purity of the present deposits. XPS determinations (see Table 2) have shown that whatever the rhodium precursors used, rhodium(0) aggregates are formed containing low amounts of impurities. Indeed, the binding energies $E\ 3d_{5/2} = 307.0\ \text{eV}$ and $E\ 3d_{3/2} = 312.0\ \text{eV}$ are in good agreement with the literature data [17]. Starting from **1**, the chlorine incorporation is only 1.5% of the total aggregate weight whereas the classical impregnation methods in our hands gave around 8%. From precursors **2** and **3** the presence of some amounts (7 and 14%) of carbon is determined, but from **3** no oxygen incorporation was noted.

Infrared and mass spectrometry determinations on complex **1–3** [18] have shown that under a helium atmosphere containing dihydrogen the Cl, CO, acac and allyl ligands are easily removed. Thus the three equations give the balance of the reactions observed:



The role of dihydrogen in the organometallic chemical vapour deposition process (OMCVD) for the activation and decomposition of precursor **1** has been recently investigated [19].

Hydrogenation experiments on 1-octene and benzene were carried out because this reaction is sensitive to the amounts of chlorine remaining on the catalyst. Results collected in Table 3 show that the Rh catalyst prepared by OMCVD (ex. [Rh₂Cl₂(CO)₄]) display a good activity for

Table 2
Relative amounts of Rh, Cl and C on the deposits determined by XPS (wt.%)

Metal complex	Deposition conditions	%Rh	%Cl	%C
[Rh ₂ Cl ₂ (CO) ₄]	He	77	23	–
	He/H ₂ ^a	98.5	1.5	–
[Rh(allyl) ₃]	He	81	–	19
	He/H ₂ ^b	93	–	7
[Rh(CO) ₂ (acac)]	He	68	–	32
	He/H ₂ ^a	86	–	14

^a Gas flows: 40 sccm for He, 10 for H₂.

^b Gas flows: 48 sccm for He, 2 for H₂.

Table 3
Catalytic tests

Catalyst	Particle size (nm)	Activity in benzene hydrogenation ^a (h ⁻¹)	Activity in octene hydrogenation ^b (h ⁻¹)
1%Rh/SiO ₂ (OMCVD)	1.8	85	1190

^a Octene hydrogenation: $P_{H_2} = 1$ bar, $T = 25^\circ\text{C}$, [substrate] = 0.145 mol, solvent: EtOH (50 ml), $[\text{Rh}]_{\text{total}} = 9.7 \cdot 10^{-5}$ mol.

^b Benzene hydrogenation: $P_{H_2} = 20$ bar, $T = 80^\circ\text{C}$, [substrate] = 0.145 mol, solvent: EtOH (50 ml), $[\text{Rh}]_{\text{total}} = 9.7 \cdot 10^{-5}$ mol.

hydrogenation of alkenes. For 1-octene, a 1% Rh/SiO₂ catalyst prepared by OMCVD, was used three times in batch experiments without any loss in activity. Other catalytic tests in carbonylation reactions under drastic conditions are under investigation.

In conclusion, the low pressure organometallic chemical vapour deposition in a fluidized bed is a convenient one-step method to easily and quickly prepare rhodium supported catalysts. Other supports have been successfully used and other metals are under investigation.

Acknowledgements

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References

- [1] M. Che and C.O. Bennett, *Adv. Catal.*, 36 (1989) 55.
- [2] B. Coq, R. Dutartre, F. Figueras and T. Tazi, *J. Catal.*, 122 (1990) 438.
- [3] J.-M. Basset, in B. Imelik, G.-A. Martin and A.-J. Renouprez (Eds.), *Catalyse par les Métaux*, Editions du CNRS, 1984.
- [4] P. Dufour, C. Houtman, C.C. Santini, C. Nédez, J.-M. Basset, L.Y. Hsu and S.G. Shore, *J. Am. Chem. Soc.*, 114 (1992) 4248, and references therein.
- [5] A.S. Gurav, Z. Duan, L. Wang, M.J. Hampden-Smith and T.T. Kodas, *Chem. Mater.*, 5 (1993) 214.
- [6] Z. Duan and M.J. Hampden-Smith, *Chem. Mater.*, 5 (1993) 994.
- [7] M. Arai, K.I. Vsui and Y. Nishiyama, *J. Chem. Soc., Chem. Commun.*, (1993) 1853.
- [8] A. Fernandez, A.R. Gonzalez-Elipe, A. Cabellero and G. Munuera, *J. Phys. Chem.*, 97 (1993) 3350.
- [9] N.L. Pocard, D.C. Alsmeyer, R.L. Mc Creery, T.X. Neenan and M.R. Callstrom, *J. Am. Chem. Soc.*, 114 (1992) 769.
- [10] A. Fernandez, A.R. Gonzalez-Elipe, E. Real, A. Cabellero and G. Munuera, *Langmuir*, 9 (1993) 121.
- [11] A. Fernandez, G. Munuera, A.R. Gonzalez-Elipe and J.P. Espinos, *Appl. Catal.*, 57 (1990) 191.
- [12] C. Dossi, A. Barstch and P. Losi, in S. Daolio (Ed.), *Advanced Syntheses and Methodology in Inorganic Chemistry*, 1991, 83.
- [13] C. Dossi, A. Borstch, A. Fusi, L. Sordelli, R. Ugo, M. Bellatrecia, R. Zaroni and G. Vlaic, *J. Catal.*, 145 (1994) 377.
- [14] K. Omata, M. Mazaki, H. Yagita and K. Fujimoto, *Catal. Lett.*, 4 (1990) 123.
- [15] S. Köhler, S. Trautmann, H. Dropsch and M. Baerns, Eurocapat-1, Montpellier (France), 12–17 September (1993) 428.
- [16] D. Geldart, *Powder Technol.*, 7 (1973) 285.
- [17] C.D. Wagner and W.M. Riggs, *Handbook of X-ray Photoelectron Spectroscopy*, Muilenberg Ed. (1987) 108.
- [18] P. Serp, R. Feurer, R. Morancho and P. Kalck, *J. Catal.*, submitted.
- [19] P. Serp, R. Feurer, R. Morancho, P. Kalck, J.C. Daran and J. Vaisserman, *J. Organomet. Chem.*, (in press).