

Letter

# Metal-organic chemical vapor deposition in a fluidized bed as a versatile method to prepare layered bimetallic nanoparticles

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## Abstract

Bimetallic supported layered nanoparticles, with an inner nucleus of platinum and an outer shell of palladium were synthesized by two successive chemical vapor deposition runs in a fluidized bed from  $\text{Pt}(\text{Me})_2(\text{COD})$  at 120°C and  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{hfacac})$  at 60°C, these remarkable mild conditions allowing in the presence of  $\text{H}_2$  to reach pure metal particles sized between 5 and 15 nm. Both TEM and EDX analyses evidenced the layered structure. The preliminary studies on catalytic dehydrogenation showed the great activity and stability of these bimetallic materials. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In the course of developing new methods to prepare heterogeneous catalysts [1], we have shown recently that combining the metal-organic chemical vapor deposition (MOCVD) process and the fluidization of porous particles was a powerful method to prepare highly divided active catalysts [2–4]. Adding small amounts of dihydrogen to the carrier gas during deposition

allowed the effective removal of the organic ligands from several volatile rhodium [2,3] and palladium [5] complexes at temperatures below 120°C, and to obtain narrow sized nanoparticles (1–4 nm). The platinum metal loading was 3.7 wt.% (theoretic 4%).

Bimetallic supported catalysts are classically prepared by simultaneous impregnation of two metal salts [6] or alternatively, from one single-source salt containing the two metals [7], by co-precipitation [1], and by ion-exchange [8]. We explored whether the MOCVD method could be extended to the elaboration of supported catalytic materials containing both palladium and platinum.

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## 2. Experimental

In an hot wall apparatus described elsewhere [2,3], small particles of platinum deposited on silica were obtained by contacting the support with a gas mixture containing helium, around 3% of dihydrogen and a  $1 \times 10^{-3}$  molar ratio of  $\text{Pt}(\text{Me})_2(\text{COD})$  (where COD is  $\eta^4$ -1,5-cyclo-octadienyl) for 3 h. The reaction was carried out at  $120^\circ\text{C}$ .

A 3.80 g charge of porous  $\text{SiO}_2$  (surface area  $170 \text{ m}^2 \text{ g}^{-1}$ ) was poured into a specific column as a fluidizable bed. The bed was heated to  $120^\circ\text{C}$  and the pressure in the column was ad-

justed to 40 Torr by introducing He as a carrier gas. The temperature of the sublimer was adjusted to  $80^\circ\text{C}$  to begin the sublimation of the precursor (0.38 g), which was carried toward the  $\text{SiO}_2$  bed by the He flow. A bubbling fluidization regime was maintained. Before the deposition area, a flow of dihydrogen was introduced to assist the precursor decomposition.

In a second step, covering the platinum particles with palladium was achieved still using the MOCVD in fluidized bed method.  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{hfacac})$  (where hfacac is the hexafluoroacetylacetonato ligand) was used, with a  $4 \times 10^{-3}$  molar ratio, under the predetermined con-

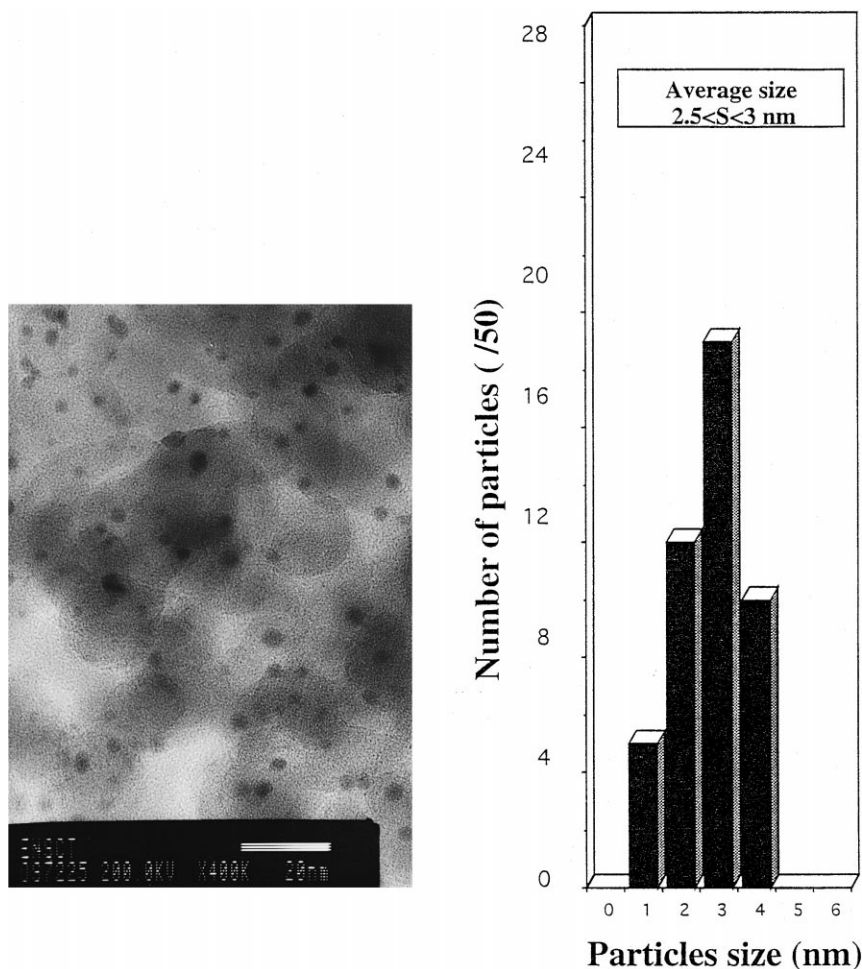


Fig. 1. Left: TEM image of platinum particles supported on silica (Pt content  $3.7 \pm 0.2$  wt.%) prepared in a first step by CVD in fluidized bed at  $120^\circ\text{C}$ , 40 Torr. Right: histogram of particle size distribution corresponding to the micrograph.

ditions adjusted for the deposition of monometallic palladium particles [4], i.e., 60°C for 2 h in the presence of 1% of dihydrogen.

A 0.30 g of the volatile complex  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{hfacac})$  was introduced in the sublimator. A 2.50 g of the previously synthesized  $\text{Pt}/\text{SiO}_2$  was poured into the column as fluidizable bed. The pressure was adjusted to 40 Torr with He as carrier gas. The sublimator was heated to 55°C, a slow flow of dihydrogen was introduced before the bed. After deposition, the material was removed from the column without any further treatment. The palladium metal loading was 3.3 wt.%.

### 3. Results and discussion

After the first deposition step, samples were set apart to characterize the material by trans-

mission electron microscopy (TEM) at 200 kV, energy dispersion analysis by X-ray (EDX), determination of metal content, and specific area measurements. Fig. 1 (left part) shows that the platinum particles are well dispersed. A narrow size distribution of particles was obtained with an average particle diameter between 2.5 and 3 nm (right part). No specific area modification was noted indicating that the microporosity of the  $\text{SiO}_2$  support was not clogged. Pure deposits were obtained with a metal loading of 3.7 wt.%.

The TEM images of  $(\text{Pt,Pd})/\text{SiO}_2$  samples, after the second step of the procedure, indicate dispersed aggregates with sizes around 5–15 nm, but with different contrast areas as shown in Fig. 2. Indeed, particles labeled 1–4 present a darker area in their core. Particles 2 and 3 are agglomerated (the grain boundary is arrow indicated in Fig. 2). EDX microanalyses show clearly that the core of the particle consists of

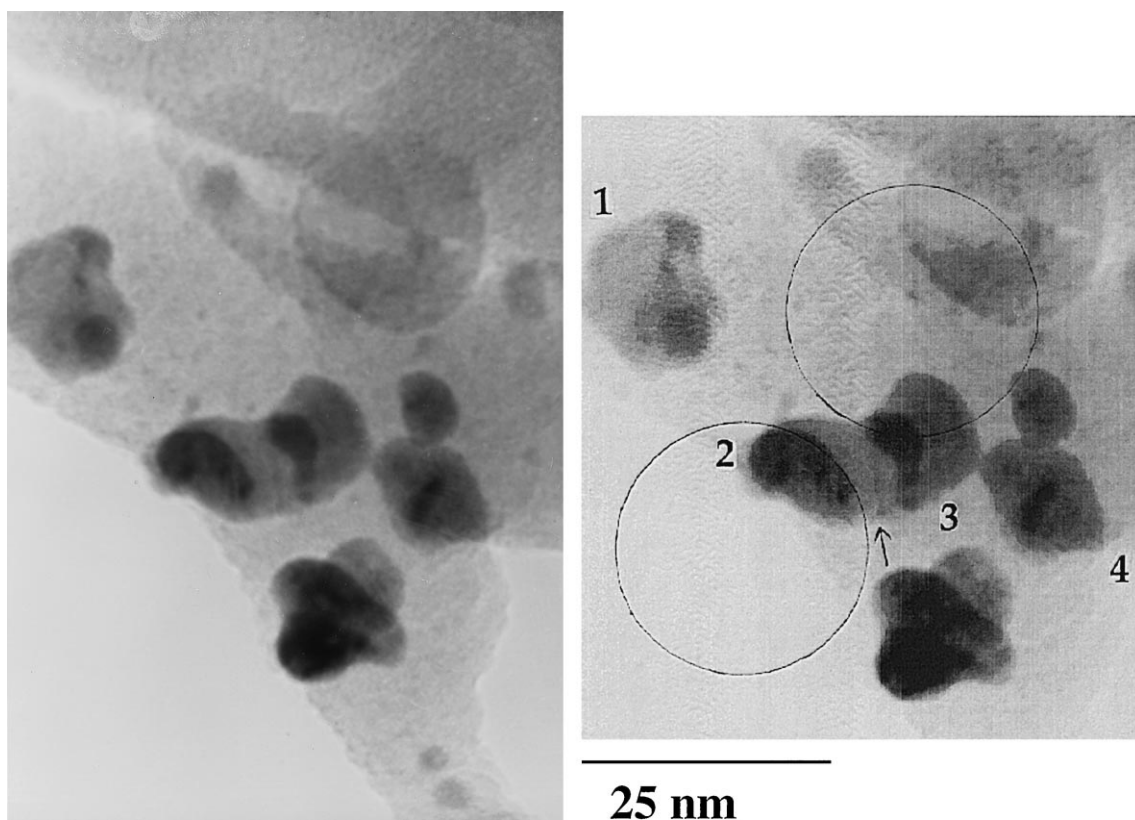


Fig. 2. Micrograph of bimetallic  $(\text{Pd,Pt})/\text{SiO}_2$  particles after the second step of palladium deposition. The darker area of each numbered particle corresponds to its Pt core.

platinum, whereas the outer area principally contains palladium. This is demonstrated by comparing the spectrum (Fig. 3a) obtained by focusing the electron beam (25 nm) on the dark core area (lower left circle in Fig. 2), with the one (Fig. 3b) recorded when the beam covers the clearer outer area (upper right circle in Fig. 2). Moreover, EDX studies on many particles show that whereas a few monometallic platinum nanoparticles were found without trace of palladium element, no palladium monometallic particles were detected. Thus, the deposition of palladium occurred exclusively on pregrown platinum sites. Micrograph in Fig. 4 (upper part) shows the same contrast phenomenon as described for Fig. 2, with a darker area in the core of the particle due to platinum. The EDX spectrum with the electron beam centered on the circled particle (Fig. 4, lower part) displays both Pd and Pt peaks indicating its bimetallic structure. The presence of fringes in the HRTEM

(300 kV) observations demonstrates that crystalline particles have been obtained.

Palladium deposition requires a lower temperature, and occurs with a higher rate than platinum deposition. Moreover, the partial pressure of hydrogen in the gas phase differs notably from palladium to platinum precursors (1% and 3% molar ratios in gas phase respectively). These remarks are very likely connected to the reactivity of palladium and/or platinum hydride species generated in the gas phase [5]. Platinum deposits presumably catalyze the deposition of palladium since palladium grows selectively on the platinum sites. Such a catalytic phenomenon was previously considered for the CVD mechanisms from noble metal complexes by several groups [5,9].

Studies concerning the dehydrogenation of cyclohexane to benzene carried out at 400°C, show a very good activity and selectivity. After four successive experiments, the particles dis-

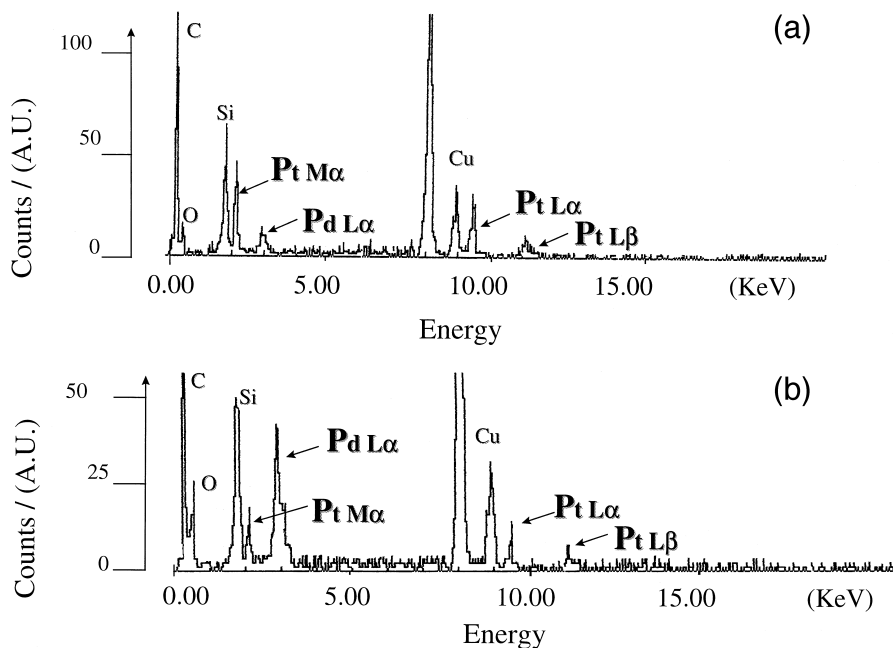


Fig. 3. EDX analysis of (Pd,Pt)/SiO<sub>2</sub> particles (Pt content  $3.7 \pm 0.2$  wt.%, Pd content  $3.3 \pm 0.2$  wt.%). Carbon and copper peaks are due to the grid support of TEM preparation. Electron binding energies in keV: C K  $\alpha_1$  = 0.280; O K  $\alpha_1$  = 0.532; Si K  $\alpha_1$  = 1.739; Cu K  $\alpha_1$  = 8.044, K  $\beta_1$  = 8.900; Pt M  $\alpha_1$  = 2.053, L  $\alpha_1$  = 9.441, L  $\beta_1$  = 11.068; Pd L  $\alpha_1$  = 2.836. (a) Analysis performed on the area corresponding to the lower left circle on Fig. 2. (b) Analysis performed on the area corresponding to the upper right circle on Fig. 2.

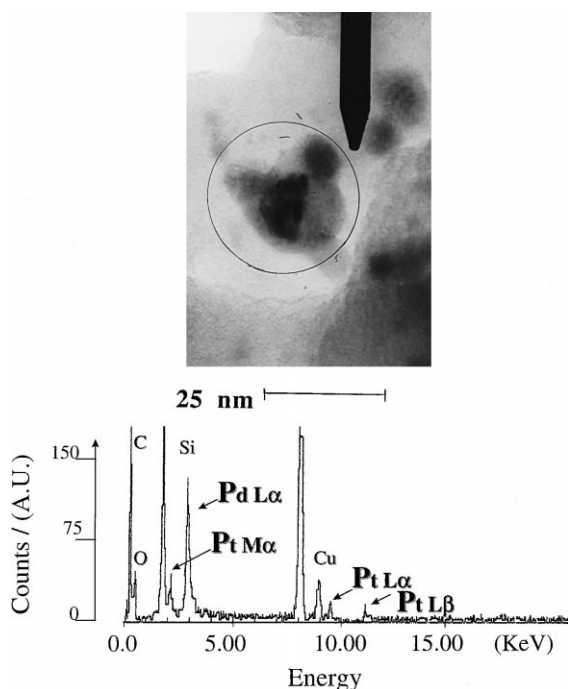


Fig. 4. Upper part: focused image of a bimetallic particle. Lower part: EDX spectrum of the whole particle showing the simultaneous presence of Pt and Pd.

play a remarkable stability of their structures. Indeed, the size and the distribution of the particles remained unchanged, and no diffusion of one metal into the other was noted.

It is worthy to note that in contrast to the alloy-like system, bimetallic particles with layered structures have been a little less widely investigated (as examples of unsupported bimetallic colloidal nanostructures, see the prior works of G. Schmid et al. and M. Harada et al. in Refs. [10,11]). However, they can serve as models for alloy formation and they could dis-

play interesting properties due to intermetallic behavior or electronic interactions. The present results show that this low temperature MOCVD process allows to prepare easily active layered nanoparticles. Investigations are carried out to develop the present method as a powerful alternative to the known methods of preparation of supported bimetallic catalysts.

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