

A New Synthetic Method toward Bimetallic Ruthenium Platinum Nanoparticles; Composition Induced Structural Changes

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The reaction of Pt(dba)₂ with Ru(COD)(COT) in various proportions under dihydrogen in the presence of PVP leads to the formation of bimetallic nanoparticles of definite compositions resulting from the relative concentration of the two complexes in the initial solution. The progressive incorporation of ruthenium into the platinum matrix leads to structural changes from face-centered cubic (fcc) for high platinum contents to hexagonal close-packed (hcp) for high ruthenium contents. For the composition Pt₁Ru₃ a contraction of the size of the particles (ca. 1.1 nm) and of the size distribution indicates the presence of a new phase consisting of monodisperse particles for which a model of truncated twinned octahedrons of 79 atoms was proposed.

The synthesis of metal nanoparticles of definite size and surface states remains a challenging problem.¹ This is even more difficult when considering bimetallic nanoparticles for which both the overall and surface composition must be controlled. However, bimetallic nanoparticles are attracting a lot of interest, particularly related to their catalytic properties.² The field has recently been reviewed by Toshima and Yonezawa.³ For example, much interest has been recently devoted to the synthesis of platinum–ruthenium nanoparticles as hydrogenation catalysts and electrochemical catalysts for fuel cell applications.^{4–7} Besides the techniques of impregnation and thermal reduction used for the preparation of heterogeneous catalysts,⁸ two new methods have been recently reported. Bönnemann et al. reported the synthesis of Pt_{0.5}Ru_{0.5} nanoparticles through co-reduction of platinum and ruthenium chlorides using NOCl₄(BHEt₃).⁶ The material consists of a 50:50 mixture of face-centered cubic (fcc) and multiply twinned decahedral very small particles (ca. 1.2 nm) and has been used as precursor for a fuel cell catalyst. Shapley et al. have used an organometallic cluster PtRu₅C(CO)₁₆ and decomposed it by a high-temperature treatment after deposition onto carbon black.⁷ This yields particles of mean size 1.6 nm and adopting a composition close to that of the precursor. An elegant in situ X-ray absorption study demonstrated the presence of a core–shell inversion during the growth process observed at temperatures between 473 and 673 K.^{7b}

In our group, we have developed a method of producing metal nanoparticles by decomposition of an organometallic precursor using a reactive gas under mild conditions.^{9,10} The advantages are the possibility to carry out the reaction in very mild conditions (room temperature or below) and therefore to obtain new structural forms of the particles as well as to control the surface composition. It has, for example, been possible to demonstrate the absence of contamination of the surface of cobalt nanoparticles using magnetic measurements.¹⁰ It was therefore of interest to determine whether this approach could

TABLE 1: Some Physical Characteristics of Mono- and Bimetallic Nanoparticles

composition	size (nm)	structure (major)	interatomic distance (Å)	CO stretch (cm ⁻¹)
Pt	1.5	fcc	2.740	2040
Pt ₃ Ru ₁	1.5	fcc	2.735	2040, 1840
Pt ₁ Ru ₁	1.5	fcc	2.715	2032
Pt ₁ Ru ₃	1.1	twinned fcc	2.704	2024
Pt ₁ Ru ₅	1.4	hcp	2.690	2017
Pt ₁ Ru ₉	1.5	hcp	2.680	2017
Ru	1.2	hcp	2.660	2013

be extended to the synthesis of bimetallic nanoparticles. Of particular interest are the possibility of obtaining a desired composition and the study of composition-induced structural changes within these nanostructures.

We describe in this communication the synthesis of bimetallic ruthenium–platinum particles of definite composition and a structural study including the changes induced by composition modification.

We have previously described the decomposition of the precursor Pt(dba)₂¹¹ (dba = dibenzylidene acetone) by H₂ or CO, in the presence of PVP (PVP = poly(vinylpyrrolidone)) to yield fcc monodisperse nanoparticles of mean size found between 1.2 and 1.6 nm, which could be modeled as constituted of closed-shell cuboctahedra.^{9b,c} In the case of reactions carried out under H₂ in the presence of PVP, monodisperse particles of 1.5 nm mean size were obtained and were modeled by a 147 atom cuboctahedron (this is a model built for the interpretation of both WAXS (wide-angle X-ray scattering) and HREM (high-resolution electron microscopy) data and does not imply the presence of a single giant cluster; nevertheless, the monodispersity of some preparations indeed suggests that definite clusters could be present in the reaction mixture). Interestingly a contraction in the Pt–Pt distance of 1.2% was observed (2.740 Å vs 2.774 Å in bulk Pt).^{9c} Similarly, the decomposition of Ru(COD)(COT)¹² by dihydrogen has been reported by our group to yield small nanoparticles of mean size found between 1 and 2 nm according to the protecting polymers (PVP or nitrocellulose).¹³ However, no structural study has been reported that

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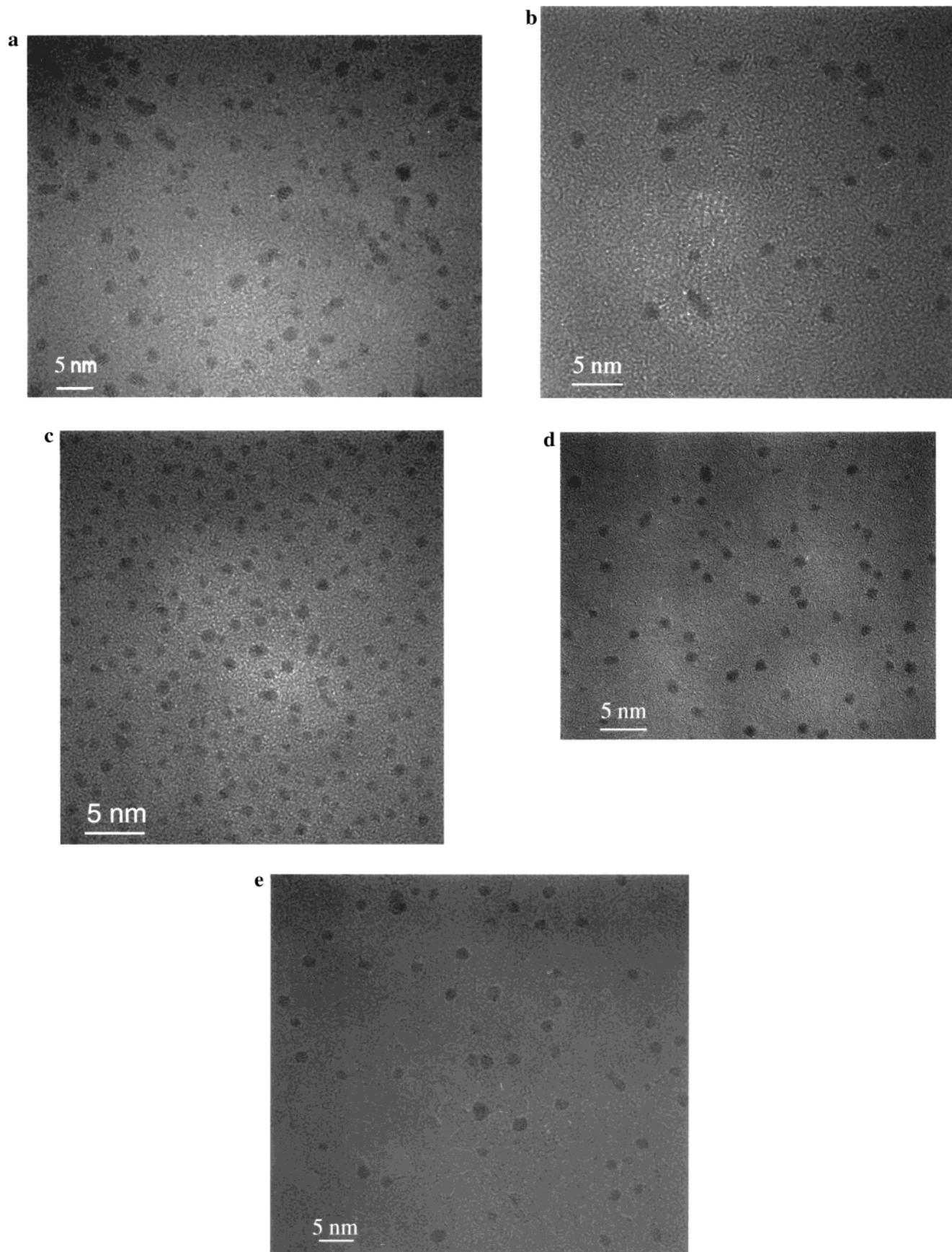


Figure 1. TEM micrograph (300 kV) of Pt3Ru1 (a), Pt1Ru1 (b), Pt1Ru3 (c), Pt1Ru5 (d), and Pt1Ru9 (e) colloids.

led to the reinvestigation of this reaction. Ru(COD)(COT) reacts with H₂ (3 bar) at room temperature in the presence of PVP for 68 h to yield a black precipitate that can be purified by

redissolution in methanol and precipitation from pentane. The resulting colloid is shown to contain 7.6 wt % ruthenium. The particles are monodisperse and display a mean size of ca. 1.2

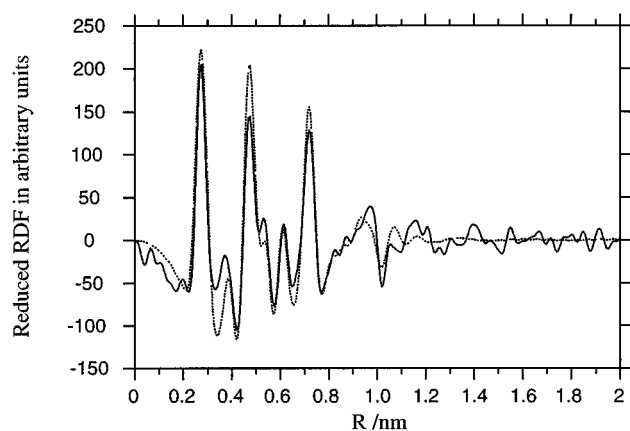


Figure 2. RDF of particles of Pt1Ru3 (solid line, experimental data; broken line, function simulated from twinned particle model)

± 0.1 nm. WAXS and HREM analysis demonstrate the presence of a hexagonal close-packed (hcp) network with a reduced metal–metal distance (2.660 Å vs 2.7058 Å in bulk Ru). A model could be built using 100 atoms arranged in an hcp network and displaying an overall spherical shape that satisfactorily reproduces the WAXS and HREM data.

The bimetallic platinum–ruthenium particles were prepared in a similar way by co-decomposition of a THF solution of the two precursors $\text{Pt}(\text{dba})_2$ and $\text{Ru}(\text{COD})(\text{COT})$, present in variable proportions, by dihydrogen at room temperature for 68 h. The various samples were treated and purified as described hereabove for ruthenium. The metal content of each colloid was determined by microanalysis (precision $\pm 5\%$ of announced value). This led to colloids incorporating respectively 3.29 wt % Ru and 19.05 wt % Pt (Pt_3Ru_1), 7.36 wt % Ru and 17.02 wt % Pt ($\text{Pt}_{1.2}\text{Ru}_1$), 12.05 wt % Ru and 8.71 wt % Pt ($\text{Pt}_1\text{Ru}_{2.67}$), 13.39 wt % Ru and 5.35 wt % Pt ($\text{Pt}_1\text{Ru}_{4.83}$), and 14.95 wt % Ru and 3.11 wt % Pt ($\text{Pt}_1\text{Ru}_{9.28}$). Each reaction was reproduced, leading to changes in overall composition and physical characteristics of little or no significance; the different colloids will be therefore named after their near stoichiometry, respectively: Pt3Ru1, Pt1Ru1, Pt1Ru3, Pt1Ru5, and Pt1Ru9 and are described hereafter (see Table 1 and Figure 1a–e).

Pt3Ru1. The particles display a size distribution centered near 1.5 ± 0.25 nm, much broader than that found for either ruthenium or platinum alone (Figure 1a). The structure of the particles is clearly fcc (WAXS and HREM data), but the metal–metal distance is shorter than in pure Pt (2.735 Å vs 2.740 Å in Pt particles).

Pt1Ru1. The particles are very similar to those of Pt3Ru1, namely a fcc structure and a mean size of 1.5 ± 0.2 nm (Figure 1b). However, the metal–metal distance is now shortened to 2.715 Å, intermediate between Pt–Pt (2.740 Å) and Ru–Ru (2.660 Å) in monometallic particles. Furthermore, ca. 20% of the particles are twinned.

Pt1Ru3. A significant decrease of both the mean particle size and the size dispersity is observed. The particles are monodisperse and display a mean size of 1.1 ± 0.1 nm. The structure is fcc but, an intriguing fact is that most ($>60\%$) of the particles are twinned. The metal–metal distance is again reduced to 2.704 Å (see Figures 1c, 2, and 3).

Pt1Ru5. The size of the individual particles (ca. 1.5 ± 0.2 nm) and their dispersity are both increased compared to Pt1Ru3 (Figure 1d). Some particles display the twinned fcc structure found in Pt1Ru3, but most of the particles (ca. 70%) are now hcp.

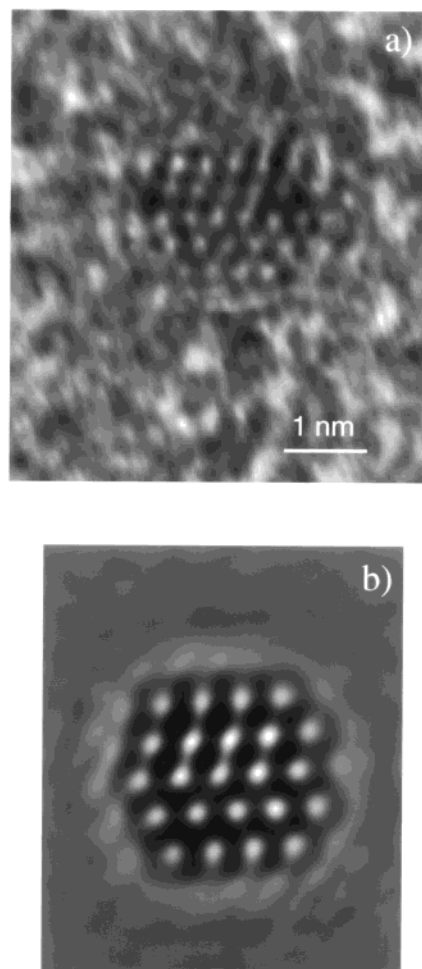


Figure 3. HREM micrograph (300 kV) of Pt1Ru3 showing the twinning (a) and image simulation (b).

Pt1Ru9. The particles all display the hcp structure but a size and a size dispersity slightly larger than pure Ru (Figure 1e).

The CO stretch of adsorbed carbon monoxide has been previously demonstrated to be a valuable probe of the oxidation state and composition of the surface of nanoparticles. Each sample has therefore been submitted to 15 min of CO bubbling, and the CO stretch was measured by infrared spectroscopy in solution in methanol. The result is shown in Table 1 and Figure 4. In a control experiment we checked that a mixture of Ru and Pt particles would lead to the observation of two bands, each one corresponding to the value found for the pure colloid. For the bimetallic system, we observe a continuous drift of the CO stretch value from that of pure platinum particles to that of pure ruthenium. This feature is surprising but has previously been observed on similar bimetallic systems.¹⁴ It results from the progressive decrease in overall surface electron density for each particle when changing from pure platinum to pure ruthenium. This does not allow us however to distinguish between a statistical alloy and a core–shell structure in which the surface platinum would feel the presence of the inner ruthenium core. In any case, this experiment strongly supports the formation of bimetallic nanoparticles and not the presence of a mixture of monometallic species.

The data described hereabove suggest a progressive incorporation of ruthenium into the fcc lattice of platinum, leading to an apparent reduction of the metal–metal distance. The apparent metal–metal distance calculated from WAXS data also shows a continuous reduction from the value found for Pt

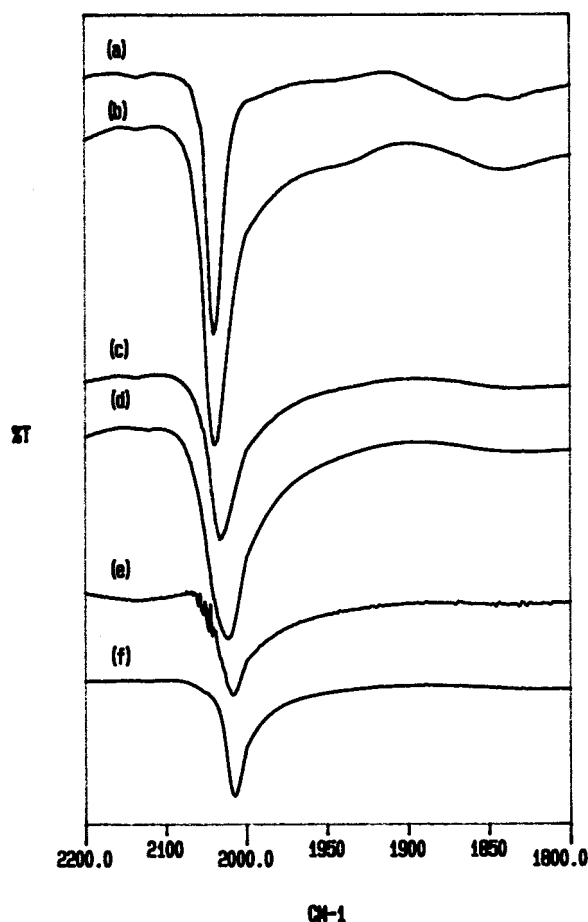


Figure 4. IR spectra (MeOH solutions) of colloids of Pt (a), Pt₃Ru₁ (b), Pt₁Ru₁ (c), Pt₁Ru₃ (d), Pt₁Ru₅ (e), and Ru (f).

nanoparticles (2.740 Å) to that found for Ru nanoparticles (2.660 Å), in agreement with a statistical distribution of both metals in the bimetallic particles. The absence of hcp particles in the mixtures up to the composition Pt₁Ru₃ and the infrared data also demonstrate the formation of bimetallic particles. For high ruthenium contents (Pt₁Ru₅ and Pt₁Ru₉), incorporation of platinum into the hcp ruthenium lattice is observed.

The most interesting observation occurs for the composition Pt₁Ru₃: a twinning is observed in the particles and is accompanied by a quasi-perfect monodispersity of the particle size (Figure 1c), which suggests a definite structure. To explain this observation, a model was built following theoretical predictions of Wales and Doye.¹⁵ The model is a truncated twinned octahedron of 79 atoms consisting of two fcc subunits assembled through a hcp base. This model was used to simulate both the radial distribution function (RDF) obtained by WAXS (Figure 2) and high-resolution micrographs (Figure 3), leading in both cases to an excellent agreement between experimental and calculated data. This twinning corresponds to the cross point between the fcc and hcp structures.

In conclusion, this study demonstrates that the mild conditions used for the decomposition of the organometallic precursors allow the synthesis of alloys of definite composition and definite structure. This is of special importance for Pt/Ru particles that may find useful applications as catalysts or electrocatalysts, the properties of which will depend on their composition. From a

structural point of view, this study allows a rare observation of the stepwise interpenetration of the fcc and hcp network. In contrast to Shapley's observations, the present data are not in favor of core-shell structures for these nanoparticles even if such structures are not entirely ruled out. However, the synthesis conditions at elevated temperature used by Shapley may explain the observed segregation. An important novel aspect of this work is the demonstration of the necessity for the particles to adopt a twinned structure in order to accommodate the presence of the two metals with a miscibility gap. This twinning occurs in definite clusters of narrow size and probably composition dispersity. More data, in particular resulting from AWAXS (anomalous WAXS) and EXAFS, are needed to fully understand the origin of this twinning; this work is presently in progress.

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