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Short communication

Preparation of Pt_{13} clusters in the presence of trialkylaluminium

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The first wet-chemical synthesis of a 13-atom platinum cluster is achieved via the decomposition of dimethyl(1,5-cyclooctadiene)platinum(II) in the presence of trialkylaluminium. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: clusters

Transition-metal nanoclusters display novel physical and catalytic properties.[1] Platinum clusters less than 1 nm in size have been prepared entrapped in zeolites via the so-called 'ship-in-a-bottle' method.[2–4] However, to our knowledge, no wet-chemical method has been reported for synthesizing free Pt_{13} clusters with a uniform particle size distribution.

Bönnemann and Richards[5] opened a novel synthetic pathway to mono- and bi-metallic nanoparticles via the 'reductive stabilization' of colloidal transition metals using aluminium trialkyls as reducing agents and colloid stabilizers. A nearly monodispersed platinum colloid with a mean diameter of 1.2 nm was obtained by reducing platinum acetylacetonate with trimethylaluminium.[6] Recently, a facile one-pot procedure was developed for dimethyl(1,5-cyclooctadiene)platinum(II), $[(1,5\text{-COD})Pt(CH_3)_2]$ (**1**).[7] This communication describes the size-selective preparation of Pt_{13} clusters by decomposing complex **1** in the presence of aluminium trialkyls.

When excess $Al(CH_3)_3$ was added to a toluene solution of complex **1**, no colour change was observed. However, upon addition of $Al(C_8H_{17})_3$ or $Al(C_2H_5)_3$, the initially colourless reaction mixture turned brown, and a black solution of colloidal platinum was obtained over the course of a few days.

^1H and ^{13}C NMR measurements were carried out *in situ* to follow the progress of the reaction and to identify the products. The first ^1H NMR spectra, recorded 30 min after the addition of $Al(C_8H_{17})_3$ or $Al(C_2H_5)_3$, revealed that extensive exchange had already occurred between the methyl groups in **1** and the alkyl groups of the organoaluminium compounds.

Spin–spin couplings to ^{195}Pt observed in the ^1H and ^{13}C NMR spectra provide strong evidence for the formation of intermediates having platinum–ethyl or platinum–octyl groups, respectively. For the platinum–ethyl groups, the methylene resonances are observed at $\delta_H = 1.76$ $[^2J(^{195}Pt, ^1H) = 91\ Hz]$, $\delta_C = 20.3$ $[^1J(^{195}Pt, ^{13}C) = 848\ Hz]$ and the methyl signals at $\delta_H = 1.41$ $[^3J(^{195}Pt, ^1H) = 80\ Hz]$, $\delta_C = 16.3$ $[^2J(^{195}Pt, ^{13}C) = 33\ Hz]$. Free 1,5-COD ethylene and were also detected in the NMR spectra and their presence was confirmed by gas chromatography–mass spectrometry (GC–MS) analyses. In the case of the reaction of complex **1** with $Al(C_8H_{17})_3$, ^{13}C NMR is much better for analysing the reaction mixture than the proton spectra because of the number of signals from the longer alkyl chains. The platinum–octyl groups were identified unambiguously: the α-carbon signal is found at $\delta_C = 28.0$ $[^1J(^{195}Pt, ^{13}C) = 845\ Hz]$. Similarly, free 1,5-COD, octane and octenes were found by NMR and GC–MS to be present in the reaction mixture.

The NMR investigations imply that the β-H elimination is the rate-determining step. When using 10 equivalents of $Al(C_2H_5)_3$ at room temperature the decomposition is very slow, and it takes more than a month for complex **1** to decompose fully. Transmission electron microscopy (TEM) analyses show that the initial particle size is around 0.7 nm.

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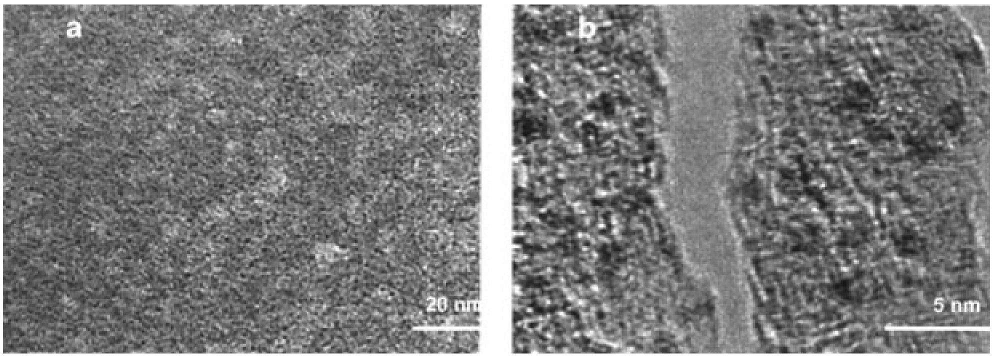

Figure 1. TEM micrographs of: (a) platinum cluster **2**; (b) platinum cluser **3** (the isolated platinum cluster embedded in aluminium oxide species).

Raising the temperature to 60 °C markedly increases the rate of reaction of the platinum–ethyl groups: the decomposition is completed within 1 h. The particle size of 0.82 ± 0.19 nm can be attributed to a bimodal size distribution, where Pt_{13} dominates along with a minor contribution of Pt_{55}.

^1H NMR spectra reveal that, at room temperature, 10 equivalents of $Al(C_8H_{17})_3$ result in complete decomposition of complex **1** within 20 h. This is much faster than the reaction with $Al(C_2H_5)_3$. TEM analyses show that very small platinum clusters (0.7 nm) are generated at the beginning of the reaction. After the decomposition has gone to completion, the platinum cluster **2** is obtained with a particle size of 0.75 ± 0.10 nm (see Fig. 1a), which corresponds to a one-shell Pt_{13} cluster. This cluster solution was found to be very stable. To isolate Pt_{13} clusters, the cluster solution as prepared above was slowly oxidized for several days. After concentrating it and drying the product under vacuum, a black powder **3** was obtained (see below for a typical Pt_{13} preparation procedure). As shown in Fig. 1b, TEM reveals that in the powder the clusters are very uniformily dispersed in aluminium oxide: the particle size remains unchanged (0.75 ± 0.12 nm). The presence of aluminium oxide was confirmed by energy-dispersive X-ray analysis.

XPS analysis was performed to characterize the valence state of the platinum cluster embedded in aluminium oxide (**3**). As shown in Fig. 2, deconvolution of the X-ray photoelectron spectrum gives binding energies of Pt $4f_{7/2}$ and Al $2p_{3/2}$ of 71.3 eV and 74.1 eV respectively, which correspond to platinum(0) and aluminium(III).

In order to identify the presence of a 13-atom platinum cluster unambiguously, the platinum LIII X-ray absorption near-edge spectrum of cluster **3** was measured and compared with theoretical model spectra (see Fig. 3) obtained using the FEFF8 code,[8] which has been shown to yield reliable results on a wide variety of sample systems, including the detailed study of effects in nanoscaled materials.[9–12] The location and intensity of shape resonances in these spectra turn out to be sensitive criteria for the completeness of shell structures. As any of the atoms in the cluster can act as the absorber atom, calculations were run for both the coordination geometries present. The resulting site-dependent spectra were then weighted according to their multiplicities and added to produce the theoretical spectrum. In order to reproduce the shoulder located at about 11 575 eV in the X-ray absorption near-edge spectrum of the cluster, it is necessary to add the spectral contribution of a centre atom with a complete shell. At the same time, the presence of backscatterers in the second coordination shell leads to the formation of a shape resonance located at 11 590 eV that is hardly observed in the cluster (see Fig. 3). Small deviations between calculation and experiment show features of both larger and smaller clusters. They may either reflect that cluster size is not described by a delta-function or reveal some influence of the stabilizing molecules.

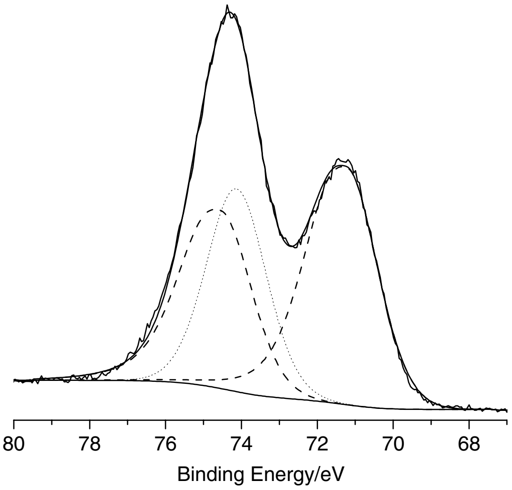

Figure 2. X-ray photoelectron spectra of Pt 4f (dashed line) and Al 2p (dotted line) for platinum cluster **3** (referenced to C 1s: 284.5 eV).

Further investigations on the size control of cluster formation and the nature of the protecting shell are in progress.

A typical procedure for the preparation of Pt_{13} clusters: $Al(C_8H_{17})_3$ (1.35 ml, 3.0 mmol) was added under argon to a

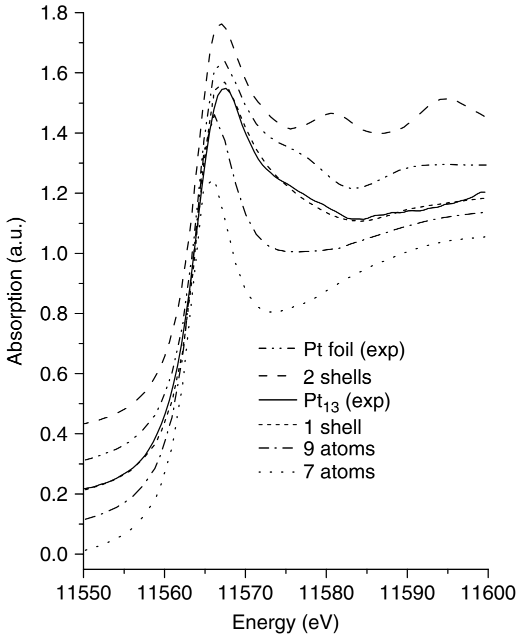

Figure 3. Platinum LIII X-ray absorption near-edge spectra of (top to bottom) platinum foil (experiment), two-shell cluster (theory), one-shell cluster [experiment (platinum cluster **3**) and theory superimposed], nine-atom cluster, and seven-atom cluster.

stirred solution of complex **1** (100 mg, 0.3 mmol) in toluene (20 ml). A black colloidal solution **2** was obtained after stirring at room temperature for 20 h. To isolate the Pt_{13} in powder form, the side-arm stopcock was opened to air for 5 days. After concentrating the sample and drying it under vacuum, a black powder **3** was obtained.

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