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Ligand-Stabilized Giant Palladium Clusters: Promising Candidates in Heterogeneous Catalysis

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Large transition-metal clusters and colloids deserve notice for different reasons. They may serve as objects for the study of quantum size effects and the formation of metallic states,¹ and they are ideal candidates for catalytic processes.² Established methods for the preparation of large metal clusters and colloids on various supports³⁻⁶ lead to a more or less broad size distribution.

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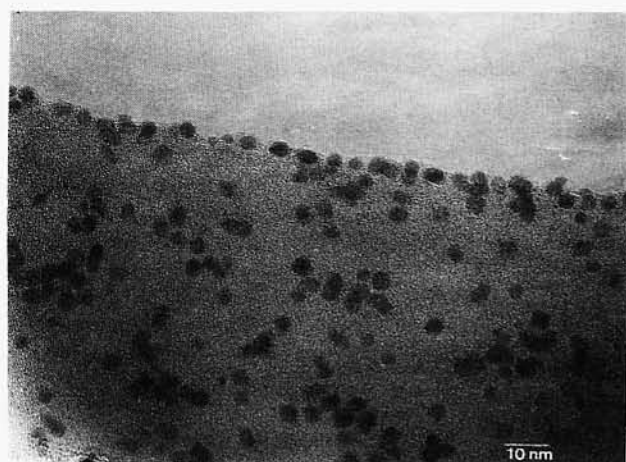


Figure 1. Mixture of Pd7/8 cluster particles.

A recent example is the synthesis of nanoscale platinum clusters in glassy carbon, showing a size range of 6–30 Å.⁷ In contrast, ligand-stabilized clusters are provided with the advantage of being predominantly uniform. The largest ligand-stabilized cluster with satisfactory characterization was described by Moiseev et al. in 1985⁸ and in a modified version by us.⁹ It is formed when Pd(II) acetate is reduced by hydrogen in acetic acid solution and in the presence of appropriate ligands, followed by the careful addition of oxygen to coordinate free surface atoms. The yields of the cluster with the idealized formula $\text{Pd}_{561}\text{phen}_{36}\text{O}_{200\pm 10}$ (phen = phenanthroline) in our synthesis is below 10%. In search of the other 90% of the palladium, we now found a mixture of mainly two different clusters with diameters of 31.5 and 36.0 Å. In a typical experiment, a solution of 2.32 g of $\text{Pd}(\text{OAc})_2$ (1.03×10^{-2} mol) and 0.25 g of phen- H_2O (0.13×10^{-2} mol) in 800 ml of acetic acid is treated with gaseous hydrogen under vigorous stirring at room temperature. In the course of 10–12 min, 2.4 moles of H_2 per mole of Pd is used, and 0.65 mole of O_2 per mole of Pd is then needed to cover uncoordinated surface Pd atoms by oxygen. It is assumed that a part of the hydrogen is dissolved in the Pd particles and is removed then by the reaction with oxygen. There is no indication (NMR) that the final products contain hydrogen. The black reaction mixture is centrifuged at 4300 revolutions per minute. Repeated washing with acetic acid and drying under vacuum gives 1.157 g of the air-stable cluster mixture (90.7%). It is soluble in a water-pyridine mixture (10:1). The filtrate of the centrifugation contains the Pd_{561} cluster, which can be isolated by addition of the 3–4-fold amount of benzene, followed by centrifugation at 5000 revolutions per minute.

By studying the particle size distribution in several electron micrographs, the sizes found were approximately 31.5 and 36.0 Å, while about 10% were smaller or bigger. Atomic resolution images, recorded at electron acceleration voltages of 300 and 400 kV and at a structural resolution of 1.6 Å, show that most of the clusters are crystalline with an almost cuboctahedral shape. The number of (111) planes of atoms are most frequently 15 and 17 (cf. Figure 1). Using the terminology of full-shell clusters, these

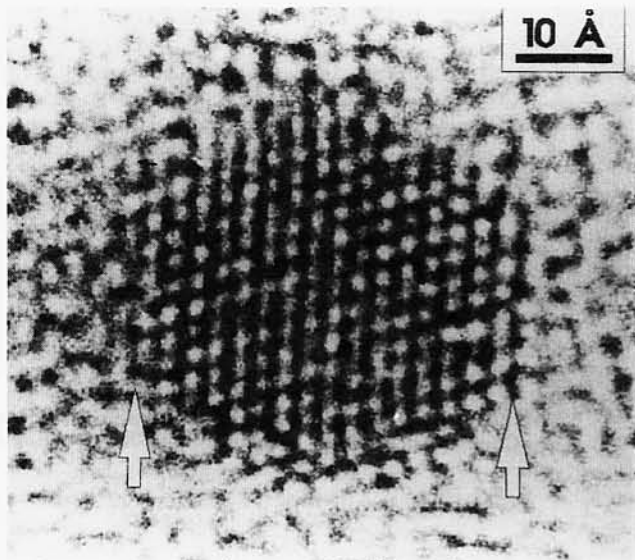


Figure 2. Cluster of palladium with 17 (111) layers of atoms. The outer layers are marked with arrows, showing the cuboctahedral shape of a cubic close packed structure. The HREM image is recorded along [110]. The cluster is supported on amorphous carbon.

numbers correspond well with seven-shell, Pd7, or eight-shell, Pd8, clusters. The images of the clusters show that the structure is most of the time the cubic close packed (fcc) type, as in the bulk metallic Pd, but structural defects occur frequently.

Figure 2 shows a single eight-shell cluster particle with an almost perfect cuboctahedral shape.

The elementary analysis¹⁰ of a microscopically investigated sample (30% Pd7, 62% Pd8) together with model studies enabled the calculation of idealized formulas for the two cluster types: $\text{Pd}_{415}\text{phen}_{60}\text{O}_{\sim 1100}$ (Pd7) and $\text{Pd}_{2057}\text{phen}_{84}\text{O}_{\sim 1600}$ (Pd8). However, as these cluster molecules are only available as a mixture, these formulas are burdened with a portion of uncertainty. Nevertheless, the experimental analytical values agree well if the microscopic evaluation is accepted. Attempts to separate Pd7 from Pd8 by means of ultracentrifugation failed as did attempts by chromatographic methods.

Not only HRTEM but also X-ray powder diffractions prove the fcc structure of the clusters. The 111, 200, 220, 311, and 222 reflexions can be observed, and their positions agree well with those of bulk palladium.

Solutions of Pd7/Pd8 are well suited to prepare heterogeneous catalysts with metal particles of two different but very similar sizes. TiO_2 adsorbs the cluster molecules up to 5 wt % spontaneously from a water-pyridine (10:1) solution. BET measurements of the undoped, 1% doped, and 5% doped TiO_2 show that the original distribution of the micropore radii (7.6–35 Å) is reduced considerably with 1 wt % of Pd7/Pd8 and has almost completely disappeared with 5 wt % of the cluster material. $\gamma\text{-Al}_2\text{O}_3$ is much less suited as a support, as only 0.3 wt % of the cluster material is adsorbed.

A novel method for catalyst preparation uses aqueous solutions of Pd7/Pd8 to hydrolyze $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in 2-propanol. $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ is precipitated together with molecularly dispersed Pd7 and Pd8. A content of 1.1 wt % as a maximum is possible. This catalyst is almost as active as if the same amount of cluster molecules were adsorbed on the surface. It may be advantageous, if it is stressed mechanically, e.g., by vigorous stirring. If the surface is damaged, then new active surfaces are continuously reformed.

Preliminary experiments with Pd7/8 on TiO_2 and Al_2O_3 show these materials to be powerful catalysts in various olefin hydrogenation reactions. Diolefins like 1,3-cyclooctadiene or dicyclo-

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(10) Analytical data calculated (found) for a microscopically investigated mixture of 30% $\text{Pd}_{415}(\text{C}_{12}\text{H}_8\text{N}_2)_{60}\text{O}_{1123}$ and 62% $\text{Pd}_{2057}(\text{C}_{12}\text{H}_8\text{N}_2)_{84}\text{O}_{1632}$: C, 4.71 (5.14 ± 0.03); H, 0.27 (0.42 ± 0.05); N, 0.91 (0.84 ± 0.02); O, 10.03 (9.98 ± 0.21); Pd, 84.08 (83.62 ± 0.11).

pentadiene can be semihydrogenated selectively. 1-Hexyne is transformed to 1-hexene with 98% yield.

All hydrogenation processes are definitely heterogeneously catalyzed, as no case has been observed where the filtered products showed catalytic activities. The activities of repeatedly used catalyst samples turned out to be absolutely constant.

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