

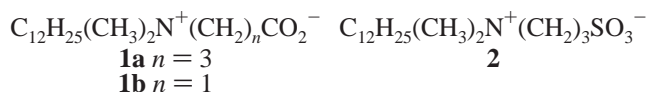
Water-Soluble Colloidal Adams Catalyst: Preparation and Use in Catalysis

Manfred T. Reetz* and Michael G. Koch

Max-Planck-Institut für Kohlenforschung,
1 Kaiser-Wilhelm-Platz, D-45470 Mülheim/Ruhr, Germany

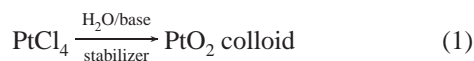
Received March 1, 1999

In 1922 Adams reported that a certain form of bulk PtO₂, prepared by the reaction of H₂PtCl₆ with NaNO₃ at 450 °C, is an excellent hydrogenation catalyst.¹ Indeed, Adams catalyst has continued to play a significant role in heterogeneous catalysis.² Platinum dispersed on solid supports such as Al₂O₃ or charcoal also constitute commercially available catalytically active systems.^{2c,2d,3} Here we report on the preparation and application of water-soluble nanosized colloidal PtO₂ stabilized by carbo- or sulfobetaines **1** or **2**, respectively.⁴



In comparison to the vast literature on zerovalent transition metal colloids stabilized by polymers, surfactants, or special ligands,⁵ much less is known concerning the corresponding nanosized transition metal oxides.⁶ A particular challenge is the preparation of concentrated solutions of water-soluble nanoparticles of metal oxides under conditions which resist agglomeration to insoluble bulk material. Such aqueous colloidal solutions would allow the practical immobilization of preformed nanoparticles in membranes or on solid supports. We have previously demonstrated that carbo- and sulfobetaines of the types **1** and **2**, respectively, are excellent water-soluble stabilizers for a number of transition metal colloids, the latter being prepared by electrochemical reduction of the corresponding metal salts in organic or aqueous medium.⁷ We therefore speculated that the corresponding metal oxide colloids could be accessible by simple hydrolysis/condensation of metal salts under basic aqueous conditions in the presence of the above surfactants.

Indeed, upon stirring an aqueous solution of PtCl₄ and carbobetaine **1a** (molar ratio, 1:4) in the presence of excess NaOH at 50 °C for 7 d, complete consumption of the yellow platinum salt was observed with formation of a deep red-brown colloidal solution of PtO₂/**1a** (eq 1). The reaction was monitored by UV-



vis spectroscopy (disappearance of the PtCl₄ absorption at 250 nm and appearance of a plasmon absorption in the range 200–800 nm) and by transmission electron microscopy (TEM). TEM analysis of the final colloid showed the presence of 1.8 ± 0.3-nm-sized particles (Figure 1). The existence of nanoparticles in solution was demonstrated by small-angle X-ray scattering (SAXS). The use of stabilizer **1b** also gave 1.8-nm-sized PtO₂ particles. The condensation process can also be performed at reflux temperature for 2.5 h with Li₂CO₃ as a base, resulting in 1.9 ± 0.4 nm PtO₂/**1b** colloids. High-resolution TEM analysis of the samples revealed the existence of lattice planes, demonstrating the nanocrystalline character of the particles, as in the case of PtO₂/**1b** (Figure 2).

The reaction could also be performed using sulfobetaine **2** and Li₂CO₃ as the base, leading to 1.7 ± 0.3-nm-sized PtO₂/**2** colloids. Other Pt(IV) salts such as H₂PtCl₆ can also be employed for the preparation of PtO₂ colloids.⁴ The addition of excess acetonitrile to the colloidal solution resulted in the essentially complete precipitation of the PtO₂ colloid as a brown solid. The precipitation

of the PtO₂/**1b** colloid afforded a solid with a platinum content of 15.2%, which is completely redispersible in water. Alternative approaches for the workup of the crude colloidal solution are a dialysis process or ion exchange.⁸ Platinum contents of more than 30% can be attained by a combination of these workup procedures if so desired.

To leave no doubt that the colloids are indeed composed of PtO₂ particles, additional methods of characterization were applied. For example, X-ray photoelectron spectroscopy (XPS)⁹ of the prepared colloids and of commercial Adams catalyst clearly showed the presence of Pt(IV) species, as demonstrated by the similarities in the Pt 4f regions. The binding energy, E_B, amounts to 74.5 eV both in colloidal PtO₂ and in Adams catalyst. Analysis of colloidal PtO₂ and commercial Adams catalyst by extended X-ray absorption fine structure (EXAFS) spectroscopy¹⁰ also gives evidence for a very similar composition and structure of the particles. For example, measurements of the PtO₂ colloid at the Pt L_{III} edge revealed an oxygen backscatterer at 2.0, 3.6, and 3.8 Å and a platinum backscatterer at 3.1 Å, with a coordination number of 6 for platinum. These values are in full agreement with those obtained for commercial Adams catalyst in the present study and those reported in the literature for pure α-PtO₂.¹¹

To test whether the preformed water-soluble PtO₂ colloids can be immobilized on solid supports quantitatively while maintaining their original size, aqueous solutions of a sulfobetaine-stabilized PtO₂ colloid (1.9 nm; 14.4% Pt) were stirred with various forms of Al₂O₃, namely Alox N (neutral),^{12a} Alox S (acidic),^{12a} and Puralox (neutral),^{12b} the ratio of colloid to solid support being chosen so as to obtain materials having about 5% platinum (by

- (1) (a) Voorhees, V.; Adams, R. *J. Am. Chem. Soc.* **1922**, *44*, 1397–1405. (b) Adams, R.; Shriner, R. L. *J. Am. Chem. Soc.* **1923**, *45*, 2171–2179. (2) (a) Adams, R.; Voorhees, V.; Shriner, R. L. In *Org. Synth. Coll.*, Vol. 1, 2nd ed.; Blatt, A. H., Ed.; Wiley: New York, 1941; pp 463–470. (b) Frampton, V. L.; Edwards, J. D., Jr.; Henze, H. R. *J. Am. Chem. Soc.* **1951**, *73*, 4432–4434. (c) Paquette, L. A., Ed. *Encyclopedia of Reagents for Organic Synthesis*, Vol. 6; Wiley: Chichester, 1995. (d) Augustine, R. L. *Catalytic Hydrogenation*; Dekker: New York, 1965. Previous work on platinum oxide catalysts: (e) Willstätter, R.; Waldschmidt-Leitz, E. *Chem. Ber.* **1921**, *54*, 4, B113–B138, and literature cited therein. (3) Ertl, G.; Knözinger, H.; Weitkamp, J., Eds. *Handbook of Heterogeneous Catalysis*, Vol. 1–5; VCH: Weinheim, Germany, 1997. (4) Reetz, M. T.; Koch, M. G. Patent applied for DE-A 19852547.8, 1998. (5) (a) Schmid, G., Ed. *Clusters and Colloids: From Theory to Applications*; VCH: Weinheim, Germany, 1994. (b) Fendler, J. H., Ed. *Nanoparticles and Nanostructured Films*; Wiley-VCH: Weinheim, Germany, 1998. (6) Examples of metal oxide colloids: (a) Lume-Pereira, C.; Baral, S.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1985**, *89*, 5772–5778. (b) Harriman, A.; Thomas, J. M.; Millward, G. R. *New J. Chem.* **1987**, *11*, 757–762. (c) Kalyanasundaram, K.; Grätzel, M. *Angew. Chem.* **1979**, *91*, 759–760; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 701. (d) Christensen, P. A.; Harriman, A.; Porter, G.; Neta, P. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1451–1464. (e) Claerbout, A.; Nagy, J. B. Preparation of Catalysts V. In *Stud. Surf. Sci. Catal.*, Vol. 63; Poncelet, G., Ed.; Elsevier: Amsterdam, 1991; pp 705–716. (f) Pileni, M. P. *Langmuir* **1997**, *13*, 3266–3276. (g) Reetz, M. T.; Quaiser, S. A.; Winter, M.; Becker, J. A.; Schäfer, R.; Stimming, U.; Marmann, A.; Vogel, R.; Konno, T. *Angew. Chem.* **1996**, *108*, 2228–2230; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2092. Examples of metal sulfide colloids: (h) Weller, H.; Eychemüller, A. Semiconductor Nanoclusters: Physical, Chemical, and Catalytic Aspects. In *Stud. Surf. Sci. Catal.*, Vol. 103; Kamat, P. V.; Meisel, D., Eds.; Elsevier: Amsterdam, 1996; pp 5–22. (7) (a) Reetz, M. T.; Helbig, W. *J. Am. Chem. Soc.* **1994**, *116*, 7401–7402. (b) Reetz, M. T.; Helbig, W.; Quaiser, S. A. In *Active Metals: Preparation, Characterization, Applications*; Fürstner, A., Ed.; VCH: Weinheim, Germany, 1996; pp 279–297. (c) Reetz, M. T.; Helbig, W.; Quaiser, S. A., EP 0672 765 A1, March 4, 1995. (8) Dialysis was performed on 0.01 M solutions of the colloids using a dialysis hose. Whereas the PtO₂/**2** colloid isolated by precipitation contains small amounts of Li (0.6%) and Cl (4.5%) in addition to Pt (13%), samples obtained by dialysis are essentially Li- and Cl-free: Li (0.02%), Cl (<0.1%). (9) We thank W. Grünert and M. Heber (Ruhr-Universität Bochum) for the XPS measurements. (10) We thank U. Kolb for the EXAFS studies. (11) (a) Hoekstra, H. R.; Siegel, S.; Gallagher, F. X. In *Platinum Group Metals and Compounds*; Advances in Chemistry Series, Vol. 98; American Chemical Society: Washington, DC, 1971; pp 39–53. (b) Muller, O.; Roy, R. *J. Less-Common Met.* **1968**, *16*, 129–146.

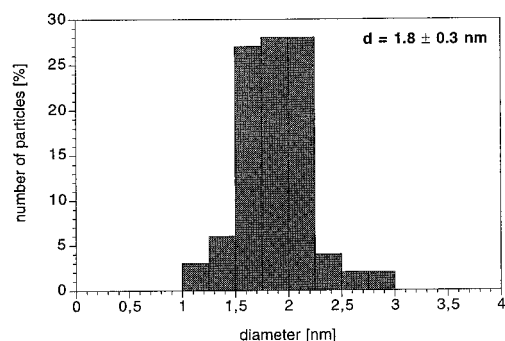
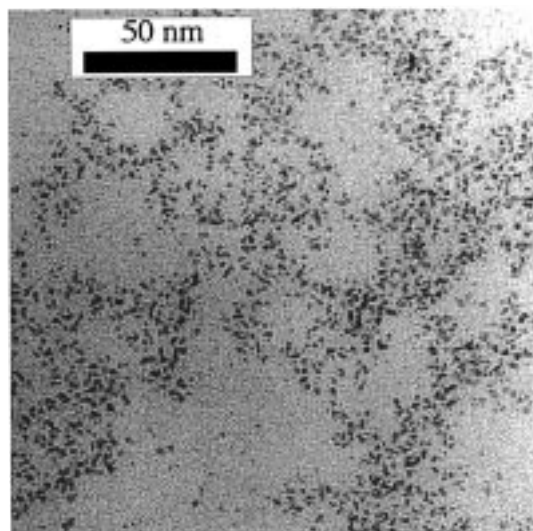


Figure 1. TEM visualization of a 1.8-nm-sized PtO₂ colloid stabilized by betaine **1a**.

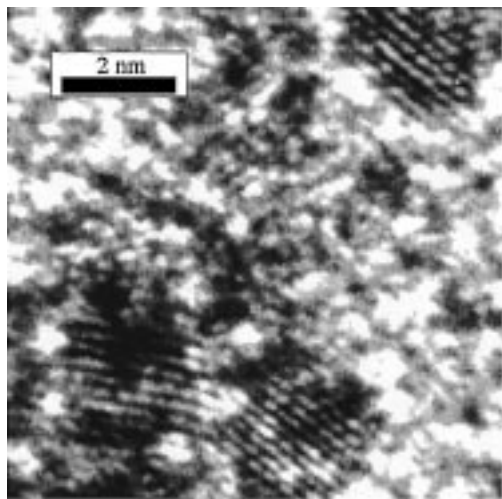
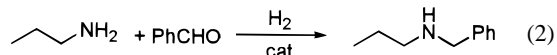


Figure 2. High-resolution TEM picture of a 1.9-nm-sized PtO₂ colloid stabilized by betaine **1b**.

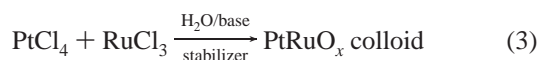
weight). After stirring for 20 h at room temperature, the mixtures were filtered. In the case of Alox S significant immobilization occurred, but the filtrate was still red-brown, indicating that the interaction between the acidic solid support and the water-soluble PtO₂ colloid is not optimal. In contrast, the filtrates in the case of the other two solid supports turned out to be completely colorless. In these cases the solid materials were washed several times with methanol to remove the surfactant. The brown samples were then dried in vacuo and subjected to elemental analysis (PtO₂/Alox N: 4.6% Pt, 0.3% N; PtO₂/Puralox: 4.7% Pt, 0.0% N). TEM analysis showed the presence of 1.9-nm-sized particles, which demonstrates that immobilization does not result in undesired particle growth. To test the new materials for catalytic

activity, the reductive amination of benzaldehyde by *n*-propylamine was chosen as a model reaction (eq 2).



Using the new catalyst PtO₂/Al₂O₃, commercially available Pt/Al₂O₃ (5%),^{12c} and Adams catalyst,^{12d} reductive amination was carried out at a substrate-to-Pt ratio of 1000:1 in methanol as the solvent at room temperature and atmospheric pressure. Catalyst activities were determined by measuring the uptake of H₂ per gram of Pt per minute. The results show that immobilized colloidal PtO₂ (1060 mL H₂ g⁻¹ min⁻¹) is about 4–5 times more active than the commercial catalysts (253 and 196 mL H₂ g⁻¹ min⁻¹, respectively). Selectivity in favor of the desired monobenzylated product is >99%. The PtO₂ colloid is also effective in the hydrogenation of carbonyl compounds or olefins, either in solution or in immobilized form.⁴

Finally, preliminary experiments directed toward the preparation of water-soluble colloidal bimetallic oxides turned out to be successful. Upon stirring the aqueous solution of PtCl₄ and RuCl₃ (1:1 molar ratio) in the presence of sulfobetaine **2** and Na₂CO₃ at 80 °C for 18 h, a black colloidal solution was obtained (eq 3).



Following purification by dialysis, the colloid was characterized by TEM, demonstrating the presence of 1.5 ± 0.4-nm-sized particles. Elemental analysis revealed 6.4% Pt and 4.0% Ru by weight, corresponding to a Pt:Ru molar ratio of about 1:1. Energy-dispersive X-ray (EDX) spot analysis proved the presence of both metals in individual nanoparticles. According to an XPS analysis,⁹ platinum occurs as Pt(II) and Pt(IV) in similar amounts in addition to Ru(IV). This means that Ru(III) reduces about 0.5 equiv of Pt(IV) to Pt(II) with formation of Ru(IV), as expected from the redox behavior of the two metals (Pt⁴⁺ + 2 Ru³⁺ → Pt²⁺ + 2 Ru⁴⁺).¹³ The PtRuO_x/2 colloid is stable for months in aqueous medium. By employing different ratios of the two metal precursors, the metal composition (Pt:Ru) of the colloids can be adjusted in the range from 1:4 to 4:1 on an optional basis. Moreover, if so desired, the colloidal Pt/Ru oxides can be converted into the corresponding zerovalent metal colloids by treating the aqueous colloidal solutions or the immobilized forms with H₂ at room temperature, while no significant changes in particle size or Pt/Ru composition occurred upon doing so.¹⁴

In summary, we have demonstrated that hydrolysis/condensation of PtCl₄ or H₂PtCl₆ under basic conditions in the presence of betaines **1** or **2** as stabilizers constitutes a simple way to fabricate water-soluble colloidal PtO₂. Such colloidal solutions are stable for months and can be concentrated up to 0.5 M. The nanoparticles can be immobilized on solid supports with formation of highly active heterogeneous (pre)catalysts. Industrial viability may pertain, especially in view of the fact that it can be extended to the production of bimetallic systems of the type PtRuO_x. Such water-soluble mixed metal oxides are candidates for chemical (pre)catalysts in organic transformations and electrocatalysts in fuel cells.¹⁵

JA9906498

(12) (a) Aldrich, BET area: 155 m²/g. (b) Condea, BET area: 221 m²/g. (c) Heraeus, BET area: 20 m²/g. (d) Heraeus, BET area: 80 m²/g.

(13) Weast, R. C., Ed., *CRC Handbook of Chemistry and Physics*, 1st student ed.; CRC Press: Boca Raton, FL, 1988.

(14) The same procedure can be applied to the PtO₂ colloids.

(15) Other approaches to the preparation of electrocatalysts: (a) Oetjen, H.-F.; Schmidt, V. M.; Stimming, U.; Trila, F. *J. Electrochem. Soc.* **1996**, *143*, 3838–3842. (b) Krausa, M.; Vielstich, W. *J. Electroanal. Chem.* **1994**, *379*, 307–314. (c) Schmidt, T. J.; Noeske, M.; Gasteiger, H. A.; Behm, R. J.; Britz, P.; Brijoux, W.; Bönnemann, H. *Langmuir* **1997**, *13*, 2591–2595. (d) Reddington, E.; Sapienza, A.; Guran, B.; Viswanathan, R.; Sarangapani, S.; Smotkin, E. S.; Mallouk, T. E. *Science (Washington, D.C.)* **1998**, *280*, 1735–1737.