

# Solvated Atoms of Platinum, Palladium and Gold

## PRECURSORS TO COLLOIDS, FILMS AND CATALYSTS

By Professor Kenneth J. Klabunde

Department of Chemistry, Kansas State University, U.S.A.

Atoms of the noble and other metals can be trapped in cold solvents, and solvated metal atom solutions can be prepared and manipulated at low temperatures. Such solvated atoms have been useful in: (a) the preparation of non-aqueous colloidal metal solutions which, in turn, can be used to prepare metallic films of platinum, palladium and gold; (b) preparing ultra-fine bimetallic powders of gold-tin; (c) trapping platinum-tin fine particles on alumina in order to prepare bimetallic Pt<sup>0</sup>Sn<sup>0</sup> heterogeneous catalysts. Ultra-fine particles of metals are usually prepared by high temperature metal salt reduction methods (1–3). Under such conditions, the approach to the most thermo-dynamically stable state has often moved further than is desirable. Very small, nano-scale particles and kinetically stable phases are often not attainable by such reduction techniques. This is particularly true of bimetallic combinations; meta-stable bimetallic particles either revert to the most thermodynamically stable state or may phase-separate under high temperature reducing conditions. In order to prepare meta-stable states or possibly new phases of nano-scale metal particles, low temperature, kinetic growth methods should be employed (4). Zero-valent atoms should be used rather than salts or oxides since reduction steps can thus be avoided. Actually, in recent years we have witnessed the development of several methods for the low temperature, kinetically controlled growth of metal clusters from free atoms. These include the gas phase “cluster beam” approach (metal clusters, Buckyballs, etc.) and the clustering of metal atoms in low temperature matrices. In order to carry out

cluster syntheses on a large scale with relatively low expense, we have studied such cluster growth in low temperature organic solvents (5). In fact this method has been practiced for about 20 years and serves as a forerunner of other clustering methods (6). Kinetic control of cluster growth can be realised, and the unique structure/reactivity of such materials has been demonstrated many times (4). Magnetic properties have also been studied (7).

In this method, metal atoms are first trapped in frozen solvents by codepositing the evaporated atoms with excess solvents at a temperature of 77 K. Upon warming, a liquid of “solvated metal atoms” is formed, often stable in the 180 to 250 K range. Further warming leads to atom agglomeration to form particles 2 to 9 nm in size, but further growth is precluded by particle solvation. Under the right conditions, stable colloidal metal solutions are formed; such as palladium particles in acetone (8).

In the presence of a catalyst support, metal atom nucleation and cluster growth occurs on the surface of the support; an example being very small platinum clusters on alumina. In this way “solvated metal atom dispersed” (SMAD) catalysts have been prepared (5).

We describe recent findings of interest to the users of platinum, palladium and gold.

### Non-Aqueous Palladium and Gold Colloids

The codeposition of palladium or gold atoms with acetone followed by slow warming leads to non-aqueous metal colloidal solutions. In the case of palladium, black solutions result whereas with gold, dark red-purple liquids are

formed (8–11). The individual colloidal particles are 4 to 9 nm in size and are indefinitely stable under the correct conditions of concentration and solvent polarity.

Polar, organic solvents can be employed, such as acetone, ethanol, isopropanol, dimethylsulphoxide and dimethylformamide (8–10).

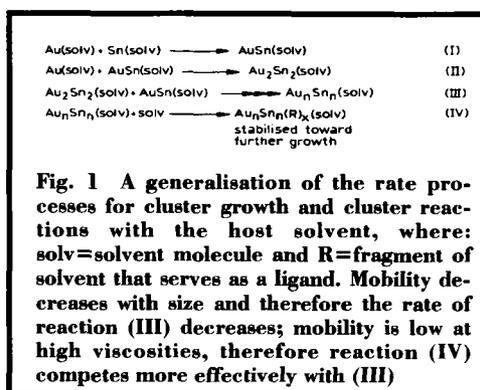
Colloid stability is apparently feasible due to the solvation/ligation effects of the solvent (steric effects), combined with electronic effects possible because of electron scavenging to form negatively charged colloidal particles (8, 11), as shown by electrophoresis studies.

Perhaps the most remarkable feature of these colloidal particles is their “living nature”. These particles will grow if their solvating medium is perturbed. Solvent removal leads to metallic films. Thus, these solutions can be “spray painted” onto surfaces. The solvent evaporates leaving films that look like palladium or gold films. The films do retain some of the organic solvent, however, which poorly affects their conductivities. Heating tends to drive out the organic impurities, and the films become smoother and better conductors (12, 13).

The best results have been obtained when surfaces that interact with the metal particles are coated. For example palladium on stainless steel, gold on copper, gold on silver, or better still, gold on polyphenylenesulphide polymer. In this case, the sulphur containing surface “ligated” well with the depositing gold particles, and upon heating a perfect, strongly adhering gold film was formed (13).

### Bimetallic Fine Particles of AuSn as a Model of PdSn and PtSn

In order to learn more about the atom-atom clustering process in solvated metal atom media, two metals were simultaneously isolated in excess cold solvents, and clustering was allowed to occur on warming. The metal pair chosen was gold/tin because these two metals form several well characterised inter-metallic compounds throughout their entire compositional range. If selectivity in growth



**Fig. 1** A generalisation of the rate processes for cluster growth and cluster reactions with the host solvent, where: solv=solvent molecule and R=fragment of solvent that serves as a ligand. Mobility decreases with size and therefore the rate of reaction (III) decreases; mobility is low at high viscosities, therefore reaction (IV) competes more effectively with (III)

was to be found, this bimetal system seemed to lend itself best to these experiments.

Experimental parameters such as evaporation rate and evaporation method, solvent polarity and viscosity, and warming rate during cluster formation were varied, and cluster/crystallite sizes were monitored. Additional information was gleaned from Mössbauer spectrometry, Differential Scanning Calorimetry (DSC), X-Ray Powder Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS) (9).

The results demonstrated that the cluster growth process was somewhat selective toward the growth of clusters of AuSn, Au<sub>3</sub>Sn and tin metal. Solvent viscosity had an effect only in cases where large viscosity changes occurred in a narrow temperature range during which cluster growth occurred (about 150–200 K). A more sensitive parameter was solvent polarity – highly polar ethanol allowed the crystallites to grow larger, to 27 nm. The most sensitive parameter, however, was the rate of matrix warming. A slow warm-up yielded smaller particles with higher surface areas, results are given in the Table. These findings can be explained by considering a competition between cluster growth and the reaction of the growing cluster with the host solvent, so that ligand stabilisation (solvation) occurs and stops further growth. In Figure 1 this is expressed as a competition between Reactions (IV) and (III).

Overall these results are promising with regard to the possibility of controlling the

Solvent Properties Compared with Surface Areas and Crystallite Sizes of Resultant AuSn Powders						
Solvent	Melting point, °C	Dielectric constant, E <sup>o</sup>	Viscosity <sup>a</sup>	Warm-up <sup>b</sup>	Surface area <sup>c</sup> , m <sup>2</sup> /g	Crystal size <sup>d</sup> , nm
Pentane	-130	1.8	0.289	fast	16.5	16.3
				slow	23.8	10.2
Acetone	-95	20.7	0.399	fast	14.9	17.8
				slow	18.3	11.2
Toluene	-95	2.4	0.772	fast	17.6	17.6
				slow	43.7	17.1
Ethanol	-117	24.3	1.733	fast	11.6	26.9
				slow	16.5	23.6
Cyclohexane	6.5	2.0	1.02 (20)	fast	19.4	13.1
				slow	28.0	12.7
Ether	-116	4.3 (20)	0.284	fast	16.6	17.8
				slow	—	9.3
Hexane	-95	1.9 (20)	0.401	fast	23.4	13.1
				slow	19.8	12.5

a Viscosities are at 0°C unless indicated otherwise in parentheses

b Fast warm-up: -196°C to 25°C in ~0.5 hours

Slow warm-up: -196°C to 25°C in 3-4 hours

c BET method using nitrogen adsorption

d From XRD data using Scherrer equation

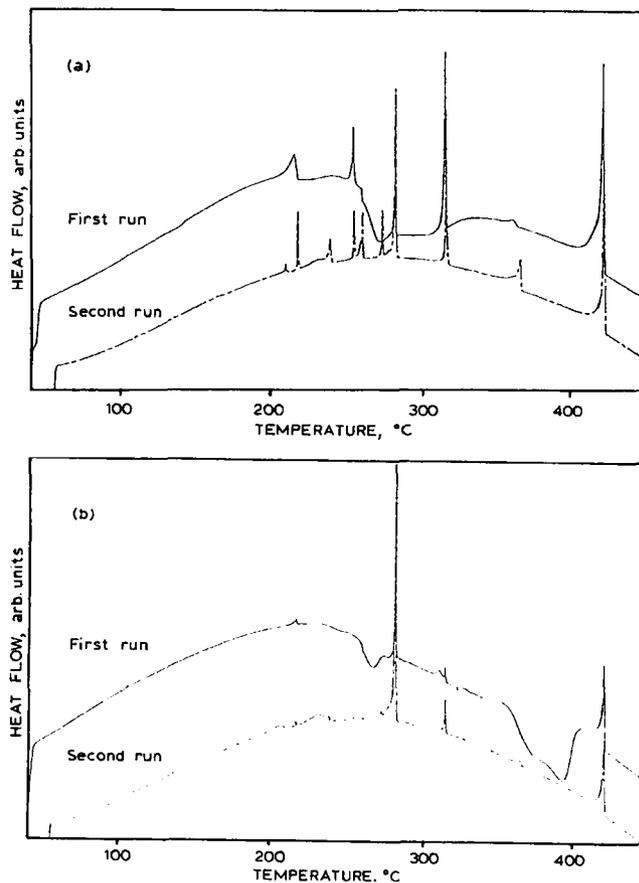
selectivity of cluster growth to certain bimetallic compositions while still maintaining a small particle size. This is demonstrated most clearly by considering Figure 2, which shows Differential Scanning Calorimetry spectra of AuSn clusters grown in acetone by fast or slow warm-up. As shown, the endothermic (upward) peaks are sharp, indicating the melting points of small particles of specific compositions (tin ~219°C, eutectic mix of Au<sub>3</sub>Sn and AuSn ~275°C, and AuSn ~419°C). Note that more selective growth to AuSn, Au<sub>3</sub>Sn and tin is evident in the slow warm-up case (b), which

is good evidence for selective growth. In the fast warm-up case (a), it is obvious that a "wilder" growth process took place leading to more components (10).

### PtSn/Al<sub>2</sub>O<sub>3</sub> SMAD Catalysts

The commercial importance of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst systems, as well as the poor understanding of the role of tin, led us to investigate this bimetallic system in some detail. These solvated metal atom dispersed (SMAD) catalysts were prepared in two ways. The "half SMAD" process refers to treating

**Fig. 2** Differential scanning calorimetry spectra of AuSn particles prepared in acetone by (a) fast warm-up and (b) slow warm-up



preformed, conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with solvated tin atoms, thereby ensuring the deposition of metallic tin on the platinum metal cluster. The “full SMAD” process refers to the evaporation/trapping/solvation of platinum and tin atoms simultaneously, followed by warming, bimetallic cluster growth and trapping on high surface area alumina (5, 14).

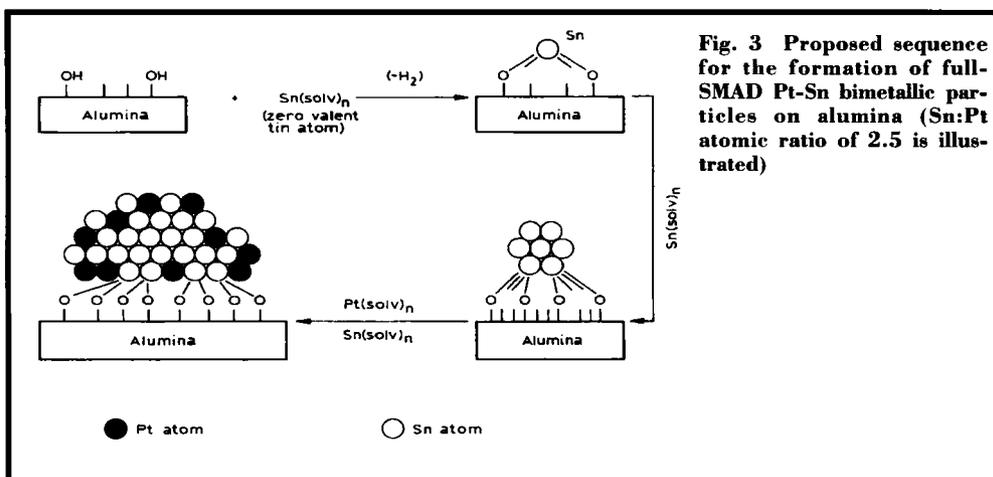
Two conventionally prepared Pt-SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were also prepared and compared with SMAD catalysts.

The unique feature of the SMAD catalysts is that Sn<sup>0</sup> is present, and the study and comparison of these Pt<sup>0</sup>Sn<sup>0</sup> systems with conventional Pt<sup>0</sup>Sn<sup>2+/4+</sup> systems should be of help in quelling the debate about whether Sn<sup>0</sup> plays a role in the commercial catalysts.

Through the combined use of catalytic

probe reactions, <sup>119</sup>Sn Mössbauer, Extended X-Ray Absorption Fine Structure, XPS and XRD it has been demonstrated that the half-SMAD catalytic particles are made up of the expected platinum particles with a partial thin Sn<sup>0</sup> coating. Interestingly, this type of catalyst showed the highest activity for n-heptane reforming to benzene and toluene.

On the other hand, the full-SMAD catalyst particles were shown to be alloy-like, probably rich in Pt<sup>0</sup> on the outer surface of the catalyst layer, Figure 3. This type of catalyst showed lower activity but better selectivity to benzene and toluene. Undesirable hydrogenolysis reactions were greatly depressed, and this is perhaps due to an ensemble effect (Sn<sup>0</sup> diluting surface Pt<sup>0</sup>) decreasing these unwanted, surface sensitive reactions.



These results also demonstrate that zero-valent tin does affect catalytic performance in beneficial ways. So, although zero-valent tin is rarely detected in conventional Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts, small amounts possibly formed on the platinum particles (by hydrogen reduction of Sn<sup>2+</sup>) may be at least partially responsible for beneficial changes in this important class of bimetallic catalysts.

A comparison of catalytic properties for the SMAD and conventional catalyst systems suggested some generalisations:

- (i) the presence of SnO<sub>2</sub> and SnO in the conventional catalysts may play a role in improving lifetime/stability by blocking platinum particle sintering;
- (ii) the presence of Sn<sup>0</sup> in combination with

Pt<sup>0</sup> can affect catalyst activity and selectivity; (iii) the presence of Pt<sup>0</sup>-Sn<sup>0</sup> alloy (rich in Sn<sup>0</sup>) can depress unwanted hydrogenolysis, while activity for the desired dehydrocyclisation is only lowered slightly (5, 14).

In summary, the use of metal vapour methods, especially solvated metal atoms, shows promise for producing ultra-fine mono-metallic and bimetallic particles for many interesting applications, including catalysts, magnetic materials, colloids and films.

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#### References

- 1 V. Haensel and R. Burwell, *Sci. Am.*, 1971, 225, 46
- 2 J. R. Anderson, "Structure of Metallic Catalysts", Academic Press, New York, 1975
- 3 R. D. Srivastava, "Heterogeneous Catalytic Science", CRC Press, Boca Raton, Florida, 1988
- 4 K. J. Klabunde, G. H. Jeong and A. W. Olsen, in "Molecular Structures and Energetics", ed. J. A. Davies, P. L. Watson, J. F. Liebman and A. Greenberg, VCH, New York, 1990, pp. 433-463
- 5 K. J. Klabunde, Y.-X. Li and B.-J. Tan, *Chem. Mater.*, 1991, 3, (1), 30
- 6 K. J. Klabunde, "Chemistry of Free Atoms and Particles," Academic Press, New York, 1980
- 7 C. F. Kernizan, K. J. Klabunde, C. M. Sorensen and G. C. Hadjipanayis, *Chem. Mater.*, 1990, 2, (1), 70
- 8 G. Cardenas-Trivino, K. J. Klabunde and B. E. Dale, *Langmuir*, 1987, 3, (6), 986
- 9 S.-T. Lin, M. T. Franklin and K. J. Klabunde, *Langmuir*, 1986, 2, (2), 259
- 10 Y. Wang, Y.-X. Li and K. J. Klabunde, "Selectivity in Catalysis: Clusters, Alloys, and Poisoning", ACS Symp. Ser., ed. S. Suib and M. Davis, in press, 1992
- 11 M. T. Franklin and K. J. Klabunde, "High Energy Methods in Organometallic Chemistry", ACS Symp. Ser. 333, ed. K. Suslick, 1987, pp. 246-259
- 12 G. Cardenas-Trivino, K. J. Klabunde and B. E. Dale, "Thin Metallic Films from Solvated Metal Atoms", SPIE Proc. (Opt. Eng. paper 821-29 (8 pages), 1987, pp. 206-213
- 13 K. J. Klabunde, G. Youngers, E. Zuckerman, B.-J. Tan, S. Antrim and P. M. A. Sherwood, invited paper for *Eur. J. Solid State Inorg. Chem.*, submitted
- 14 Y.-X. Li and K. J. Klabunde, *J. Catal.*, 1990, 126, 173