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The Formation of Supported Bimetallic Clusters: The Effect of Support - Metal
Precursor Interactions.

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Final Report

During the past four years we have studied preparative variables which affect the surface composition of supported bimetallic clusters. In particular we have focussed our attention on metal precursor-support interactions in the preparation of model supported Pt - Ru bimetallic clusters. In performing these studies we have concluded that in addition to thermodynamic considerations which stress the importance of enthalpies of sublimation in predicting the surface enrichment of one metal in preference to the other, a kinetic effect which predicts surface enrichment in the metal whose precursor interacts more weakly with the support must also be considered. Central to this model, it is envisioned that the metal whose precursor interacts more strongly with the support anchors the bimetallic cluster. The second metal is then deposited on the surface of the metal which anchors the cluster. If pretreatment temperatures are such that thermodynamic equilibrium is not achieved, the surface composition may be quite different from that which would be expected on the basis of an equilibrium thermodynamic phase diagram.

To substantiate these ideas, supported Pt - Ru bimetallic clusters were prepared using three different sets of metal precursors as follows:

- (1) $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ Because the speciation of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ is predominantly cationic and that of H_2PtCl_6 is anionic, RuCl_3 is more strongly bound to the surface of silica which is negatively charged at the pH used during synthesis. On this basis one would predict surface enrichment in Pt because its anionic precursor is repelled by the negatively charged oxide support. The results of a series of studies are consistent with this hypothesis (1-3).

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(2) Pt(NH₃)₄(NO₃)₂ and Ru(NH₃)₆Cl₃. Because the speciation of both precursors is cationic, both precursors should be strongly bound to the surface of silica provided that a strong negative charge can be generated on the surface. These conditions can be met by buffering the solution to a pH of 9.0 during preparation. Under these conditions, the surface enrichment in Pt was not nearly as large as that observed when H₂PtCl₆ and RuCl₃ were used (4).

(3) Pt/SiO₂ Sequentially Impregnated with Ruthenocene (biscyclopentadienyl ruthenium)

Under these conditions the surface was shown to be strongly enriched in Ru. However, heat treatments in excess of 500°C reversed this enrichment (5). The intraparticle reaction,

was observed to occur. In the above equation (b) stands for bulk and (s) for surface.

Several "in-situ" techniques were developed during the course of this study in order to aid in the characterization of the bimetallic clusters. The highlights of these techniques are briefly summarized below:

I. Chemisorption and Surface Composition Measurements

A pulse titration technique which enabled us to measure the surface composition of supported Pt - Ru catalysts was developed and successfully used (1,3, 6-7). The technique is based on the titration of a monolayer of chemisorbed oxygen by CO to a CO₂ end point. The stoichiometry of the titration is:

For this surface reaction the required CO/O₂ ratio is four. The corresponding reactions for Ru are considerably more complex and correspond to the following stoichiometry:

The CO/O₂ ratio corresponding to this titration is one. Because of the very different CO/O₂ titration ratio observed for Pt and Ru, the average surface composition can be easily obtained.

II. In-Situ Diffuse U.V. Reflectance Spectroscopy

To obtain "in-situ" chemical information during precursor pretreatment, "in-situ" U.V. diffuse reflectance spectroscopy was used. A special U.V. reactor-cell was constructed and was interfaced to the U.V. spectrometer through fiber optic cables and an integrating sphere (2). Using this instrumentation several important conclusions were obtained as follows: (i) The metal precursors were adsorbed on the support without incurring major modification to their structure (4); (ii) During the reduction of Pt(NH₃)₄(NO₃)₂ an intermediate surface species having the structure [Pt(NH₃)₂(H)₂]⁰ was identified (8), (iii) Mixed oxidation states of Ru were identified during the reduction of Ru(NH₃)₆Cl₃ (8) and, (iv) Lattice oxygen was incorporated into the coordination sphere of Ru to form a Ru nitrosyl which resisted reduction temperatures of 200°C in H₂ (8).

III. EDXS Studies

The elemental analysis of individual bimetallic clusters was performed using energy dispersive X-ray analysis spectroscopy (4,9). In these studies a VG 501 transmission electron microscope equipped with a field emission gun capable of focussing the electron beam to a diameter of 15 Å was used. Of particular interest was the finding that small particles were Ru rich and that large particles were Pt rich. Some excellent correlations were obtained (4).

IV. Catalytic Reactions

The well characterized supported bimetallic clusters prepared in this study were evaluated using catalytic reactions which are well understood. The hydrogenation of benzene and the hydrogenolysis of propane were found to be very sensitive to surface composition. A marked synergism was observed over bimetallic particles with adjacent dual metal sites. When bimetallic particles were not formed, this synergism was not observed (5).

V. Differential Scanning Calorimetry

A differential scanning calorimetric technique designed to measure the enthalpy of gas-solid reactions was developed (10). This technique was extended to include adsorbed surface species (11). Of particular significance in these studies was the identification of PtCl_4 as a precursor in the formation of Pt (11). When the catalysts were predried in air at 150C, PtCl_4 was quantitatively formed from $[\text{PtCl}_6]^{2-}$.

The technique was also used to quantify the heats of formation of Pt-Ru clusters (11). These heats of formation were exothermic over the entire range of compositions studied.

VI. Other Techniques

The use of XPS and X-ray fluorescence spectroscopy were used to establish that pretreatment of bimetallic clusters at temperatures in excess of 500C results in the thermodynamic equilibration of the clusters (5) (see reaction 1). High Resolution Scanning Transmission electron microscopy was used to establish both the shape and the morphology of the supported metallic particles (4).

In summary, considerable progress has been made in understanding the variables which affect the surface composition of supported bimetallic particles. We have reached the stage where it is now possible to tailor make supported bimetallic Pt-Ru clusters with well defined surface compositions. It is hoped that in the future it will be possible to extend these studies to include supported bimetallic clusters of industrial importance. For example, the preparation of supported Pt-Re and Pt-Pd-Rh catalysts having well defined surface compositions is now approachable through the judicious control of synthetic variables.

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