Evidence for Formation of Aggregates of Platinum(II) Complexes Anchored on Phosphinated SiO_2 by High-resolution Electron Microscopy

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Aggregates of ~ 8 Å size located not on the SiO_2 surface but on 'stems' and uniformly distributed on the support have been found by electron microscopy in samples containing platinum(II) complexes anchored on phosphinated SiO_2.

One aim of efforts to prepare anchored metal complexes is to obtain an immobilized surface similar to that of soluble complexes (homogeneous catalysts). Typical objects of many studies in this area are metal complexes on phosphinated silica, containing surface ligands of the type **Si**–$[CH_2]_nPR_2$ (**Si** =Si atom bonded to the hydrocarbon chain of a ligand and attached to the SiO_2 surface). It has been assumed previously that molecules of complexes are uniformly distributed on the surface upon anchoring complexes on such surface ligands. However, earlier[1] indirect evidence was found that in reality anchored complexes are located on a modified SiO_2 in the form of aggregates of molecules ('islands'). With the use of high-resolution electron microscopy we have now succeeded in observing directly the formation of an island-type distribution in anchored platinum(II) complexes.

The phosphinated SiO_2 used was prepared by treating SiO_2 with $(EtO)_2Si([CH_2]_3PCy_2)_2$ (Cy = cyclohexyl) as previously described.[2] The phosphorus content in the material obtained was 1.2×10^{-4} g-atom/g SiO_2. The phosphinated silica was treated with a solution of $(PhCN)_2PtCl_2$ in acetone for 24 h complex at room temperature. The excess of soluble Pt^{II} complex was washed out by acetone. Samples were dried at 70 °C and 3×10^{-2} Torr. The preparation and sampling of the anchored complexes were performed without contact with air. The atomic ratio P : Pt in the samples was 2.5 : 1.

The electron microscopic studies were carried out using a JEM–100CX instrument with a lattice resolution of 2 Å. The operating voltage was 100 kV and spherical aberration coefficient 2.8 mm. The values of aperture and defocus were nearly optimum (0.25 $Å^{-1}$ and −1200 Å, respectively, see ref. 3). Specimens were prepared by suspending in ethanol over holey carbon films.

Figure 1 shows the results obtained. Against the background of SiO_2 globules contrasting (spot) images of 6—8 Å size are seen, which are uniformly distributed on the SiO_2 surface. The most interesting picture is seen near the edges of the support globules. The dark spots are not lying on the surface of globules but are located at some distance on 'stems.' Images of the 'stems' have poor contrast, but we assume that the 'stem' image obtained most accurately fits the object morphology. This problem requires care in interpretation, but the out-of-focus settings and the aperture of the objective lens were chosen to be as close to optimum as possible. The width of 'stem' bases at the SiO_2 surface is 10—20 Å. The sizes of the

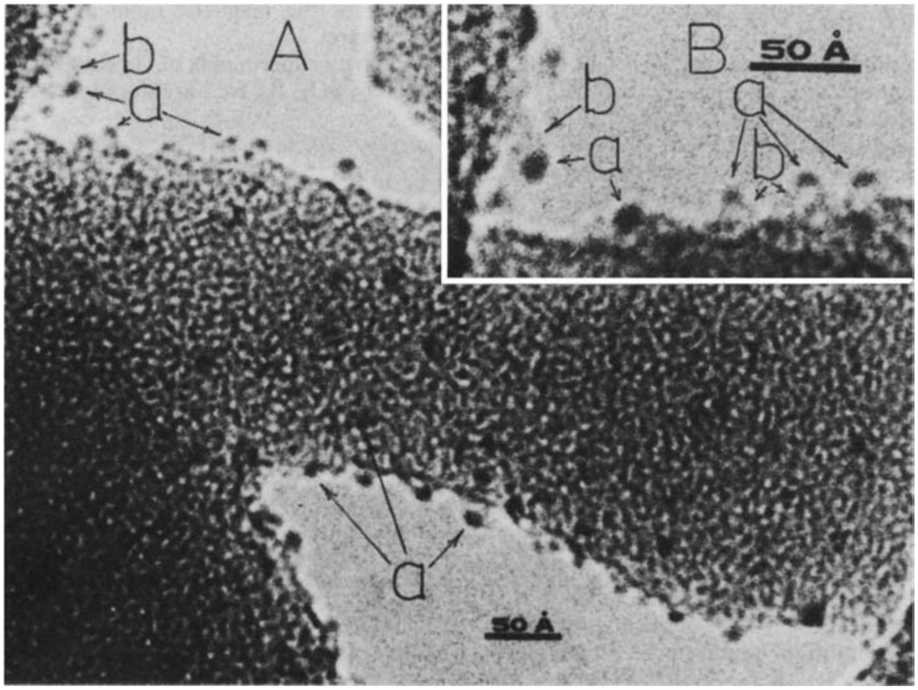
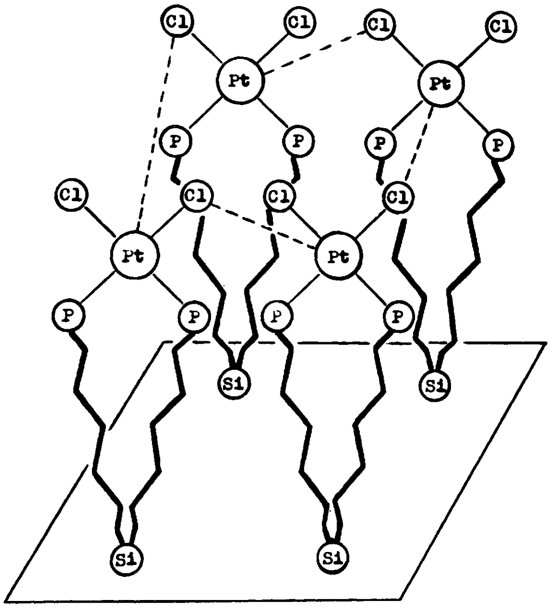


Figure 1. T.E.M. image of a sample containing $PtCl_2$ on phosphinated silica. Magnification: (A) 2 000 000×; (B) 3 000 000×. (a) Images of high contrast, corresponding to anchored Pt aggregates; (b) images of poor contrast, corresponding to the 'stems'.



$Si—P = Si\text{-}O\text{-}\mathbf{Si}[CH_2]_3PR_3$

Figure 2. A model for aggregates of anchored Pt complexes.

dark spots vary possibly owing to variation in size of the surface Pt^{II} aggregates. However, during the exposure, fast (few times per second) oscillations of aggregates with amplitudes of some Å were observed, the particles remaining attached to the same site of the surface. Since these oscillations cause diffusion of the image, the spots may correspond exclusively to particles of ~8 Å size. The distances from the centre of spots to the edge of SiO_2 globule (the height of the 'stems') are in the range 10—15 Å, corresponding approximately to the distance between the surface oxygen atom and metal atom in the fragment $Si\text{–}O\text{–}\mathbf{Si}[CH_2]_3P\cdots M$. Hence, a 'stem' may be an image of the bundle of hydrocarbon chains bonding the Pt complex with the support surface. The oscillations of the attached particles relative to SiO_2 surface may be due to thermal motion of the chains of the surface ligands.

Thus, by electron microscopy it was possible to observe directly ultra-dispersed Pt^{II} aggregates bonded to the SiO_2 surface with phosphine ligands.

Estimations according to the literature[3] show that a single Pt atom observed using the instrument employed in this work gives an image corresponding to ~3 Å in size, so the fact that the spots are ~8 Å in size shows that the aggregates contain several metal atoms. On average in a region of the support of dimensions 100 × 100 Å^2 there are 5—6 spots. Taking into account the content of Pt in the sample, this means that each aggregate contains 5—6 platinum atoms.

These 'aggregates on stems' might have been formed because of the 'island'-type distribution of surface ligands. This type of distribution on the surface of a modified silica was observed and discussed earlier.[1,4] Platinum complexes anchored on one 'island' interact with each other to produce structures shown in Figure 2, which show transmission electron microscopy (T.E.M.) images corresponding to aggregates on stems. There exists a correspondence between the T.E.M. and spin-label data; the 'stem' width (~20 Å) is close to the diameter of the 'islands,' and the average distance between the 'stems' is close to the distance between the 'islands' estimated by the spin-label technique.[1]

The conclusion about the 'island'-type distribution of anchored complexes may be important for describing the nature of active centres in catalysts containing heterogenized complexes. For example, in liquid-phase reactions such complexes may show catalytic properties similar to those of individual metal complexes in solution because aggregates of complexes are destroyed during solvation of metal ions. However, in gas-phase reactions the formation of aggregates may provide the possibility of chemisorption and substrate activation of polynuclear centres and so be a reason for the specific (compared to soluble complexes) reactivity and catalytic properties.

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