

## Study of the Distribution of Metals on the Surface of Polymer-bound Palladium(II) Complexes by X-Ray Photoelectron Spectroscopy

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**Summary** The distribution of metals on the surface of aminated polystyrene-bound palladium(II) complexes was found to be constant and independent of the metal loading by X-ray photoelectron spectroscopy.

THERE have been many recent studies on the preparation and use of polymer-bound complex catalysts.<sup>1</sup> The characterisation of the catalysts has, however, remained obscure because of the limited techniques that can be applied to such studies. Although the distribution of the metals within the polymer complex beads and on the surface of the beads is thought to play an important role in their catalysis, the distribution has only been investigated using microprobe analysis.<sup>2</sup>

X-Ray photoelectron spectroscopy (XPS) is known to be one of the best techniques for the determination of surface composition of solids. Therefore, we have applied this technique to the investigation of the distribution of metals on the surface of aminated polystyrene-bound palladium(II) catalyst beads as a function of the metal loading.

Poly-4-dimethylaminomethylstyrene (**1**) (1.40 mmol of N per g of polymer) and poly-4-pyrrolidinomethylstyrene (**2**) (1.33 mmol of N per g of polymer) were prepared by the reaction of chloromethylated polystyrene beads (2% DVB, 100–200 mesh, 1.34 mmol of Cl per g of polymer) with excess of dimethylamine and pyrrolidine, respectively.<sup>3</sup> Bisbenzotriledichloropalladium reacted with the polymers in acetone at 40 °C to give brown polymer beads, neither of which showed C≡N i.r. stretching bands. The XPS spectral data of the polymer complexes are in the Table. The XPS spectra were taken on a Hitachi 507 photoelectron spectrometer with a cylindrical mirror analyser using Al-K<sub>α</sub> radiation at ca. 10<sup>-6</sup> Torr pressure. The beaded samples were dispersed on a stainless surface and no further treatment was undertaken to clean the samples. For a series of polymer complexes, the widths at half maximum intensity of the C 1s, Pd 3d<sub>3/2</sub>, Pd 3d<sub>5/2</sub>, Cl 2p, and N 1s peaks were ca. 2.5, 2.7, 2.4, 3.4, and 3.3 eV, respectively. Typical counting rates for the C 1s, Pd 3d<sub>3/2</sub>, Pd 3d<sub>5/2</sub>, Cl 2p, and N 1s peaks were 1376, 229, 379, 211, and 47 count s<sup>-1</sup>, respectively, for the complex having the ligand (**1**) and Pd/N = 1

TABLE. XPS data for palladium complexes.

Ligand <sup>a</sup>	Pd/N	Binding energy/eV <sup>b</sup>				Peak intensity ratio		
		Pd 3d <sub>3/2</sub>	Pd 3d <sub>5/2</sub>	Cl 2p	N 1s	Pd 3d/C 1s	Cl 2p/Pd 3d	N 1s/Pd 3d
(1)	0.3	343.8	338.5	199.4	402.0	0.44	0.48	0.081
(1)	0.4	343.6	338.4	199.3	401.8	0.45	0.45	0.098
(1)	0.5	343.7	338.4	199.2	401.9	0.44	0.43	0.097
(1)	0.7	343.6	338.4	199.4	402.1	0.43	0.46	0.094
(1)	1.0	343.7	338.3	199.2	401.9	0.43	0.44	0.099
(2)	0.3	343.5	338.2	199.2	401.7	0.48	0.38	0.079
(2)	0.5	343.6	338.2	199.1	401.4	0.53	0.38	0.078
(2)	0.7	343.6	338.3	199.3	401.8	0.55	0.39	0.075
(2)	1.0	343.5	338.1	199.1	401.8	0.51	0.36	0.079
PdCl <sub>2</sub> <sup>c</sup>		343.6	338.1	199.3			0.40	
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>c</sup>		343.6	338.3	198.6			0.35	

<sup>a</sup> (1) = poly-4-dimethylaminomethylstyrene; (2) = poly-4-pyrrolidinomethylstyrene. <sup>b</sup> The binding energy values are referenced to carbon 1s (285.0 eV), and the energy differences were determined with an accuracy of  $\pm 0.2$  eV. <sup>c</sup> Reference 4.

(see Table). The Pd 3d binding energies for all the polymer complexes were almost constant and independent of the metal loading, and are similar to those for bivalent palladium complexes. Also, no appreciable difference in the Pd 3d binding energies was observed with different polymer ligands. Although all the chlorine atoms in the polymer complexes are present in the form of terminal Pd-Cl bonds ( $\nu_{\text{PdCl}}$ : 334 cm<sup>-1</sup>), the chlorine 2p binding energies are similar to that for PdCl<sub>2</sub>. The peak intensity ratios Pd 3d/C 1s, Cl 2p/Pd 3d, and N 1s/Pd 3d are almost constant for the complexes of (1) or (2), and do not depend on the metal loading. This shows that the surface composition

for the polymer complexes is almost constant and that a Pd species having the same composition is formed independent of the metal loading.† It appears that the complexation of soluble metal ions with polymer ligands does not occur uniformly within the polymer bead as a whole, but proceeds gradually from the surface of the bead towards the centre.

The fact that the surface composition of polymer complexes does not depend on the metal loading, is important in the study of catalysis of polymer-bound complexes.

(Received, 25th April 1978; Com. 433.)

† We think that the Pd species is a three-co-ordinate complex with one amine group and two atoms of chlorine.

<sup>1</sup> For reviews, see J. C. Bailar, Jr., *Cat. Rev.-Sci. Eng.*, 1974, **10**, 17; J. I. Crowley and H. Rapoport, *Accounts Chem. Res.*, 1976, **9**, 135.

<sup>2</sup> R. H. Grubbs and E. M. Sweet, *Macromol.*, 1975, **8**, 241; E. S. Chandrasekaran, R. H. Grubbs, and C. H. Brubaker, Jr., *J. Organometallic Chem.*, 1976, **120**, 49.

<sup>3</sup> K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 1953, 4097.

<sup>4</sup> M. Terasawa, K. Kaneda, T. Imanaka, and S. Teranishi, *J. Catalysis*, 1978, **51**, 406.