Composition-Size Diagrams of Supported Pt-Sn Catalysts

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Bimetallic catalyst nanoparticles are often assumed to be identical in composition with the only difference among particles being a variation in particle diameter. Analytical electron microscopy of individual particles showed this assumption to be incorrect in the case of Pt-Rh catalysts [1], and the same appears to be true for Pt-Sn particles. By plotting a scatter diagram of composition versus size for about 100 individual nanoparticles, separate phases can be identified. In the present work such composition-size diagrams are applied to Pt-Sn nanoparticles supported on γ-Al_2O_3, MgO, and modified hydrotalcite.

The Al_2O_3 and MgO catalysts were prepared by impregnating the supports to incipient wetness with an aqueous solution $SnCl_2 \cdot 2H_2O$ followed by drying 12 h in air at 110°C, wet calcining 2.5 h at 550°C, followed by calcination in dry air for 2 h at 550°C. The purpose of the wet calcination was to remove Cl left by the metal salt. Impregnation of Pt from $H_2PtCl_6 \cdot 6H_2O$ solution was followed by drying and calcination under the same conditions as for the Sn impregnation. The modified hydrotalcite catalyst was prepared by coimpregnation. Fresh catalysts were reduced for 2 h at 600°C.

Analysis of sub-5-nm particles required a field-emission scanning transmission electron microscope (VG Microscopes HB-603) fitted with a windowless Si(Li) x-ray detector (Oxford/Link Systems) operated at 300 kV [2]. Catalyst powder of Pt-Sn/support was ground in a mortar and pestle, and the finest shards were dry dispersed on carbon films on Ti TEM grids. Particle sizes were measured from annular dark-field (ADF) images at 2-5 Mx magnification (FIG. 1). Compositions of individual particles were determined from the intensities of Pt L and Sn L x-ray peaks (FIG. 2) by employing the standard Cliff-Lorimer method [3,1].

Composition-size diagrams were plotted for sample populations of Pt-Sn nanoparticles on the various support materials. FIG. 3 shows a series of composition-size diagrams for fresh and reduced Pt-Sn particles on the three supports. With the exception of particles on the MgO support (too few analyses), the composition-size diagrams of the fresh catalysts show a separate phase of Sn-rich particles distinct from the group of Pt-rich particles. For particles supported on γ-Al_2O_3, this Sn-rich phase persisted even after reduction; whereas, it was not present for the reduced catalysts when Mg was present in the support (MgO and modified hydrotalcite). Using FIG. 3 data for the reduced catalysts, an "EDX dispersion" was calculated for the γ-Al_2O_3 sample that correlated well with CO chemisorption dispersion measurements. For the MgO-containing supports, the EDX dispersion was several times higher than the measured CO chemisorption dispersion. This effect may be explained by a strong metal support interaction (SMSI) that alters CO adsorption on Pt surface atoms [4].

References

1. R. E. Lakis et al., *J. Catal.* 154 (1995) 261.
2. C. E. Lyman et al., *J. Microsc.* 176 (1994) 85.
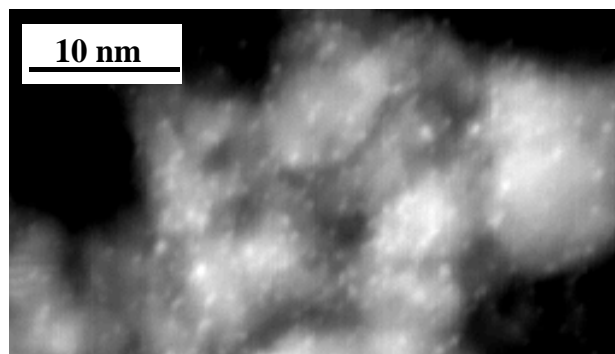3. G. Cliff and G. Lorimer, *J. Microsc.* 103 (1975) 203.
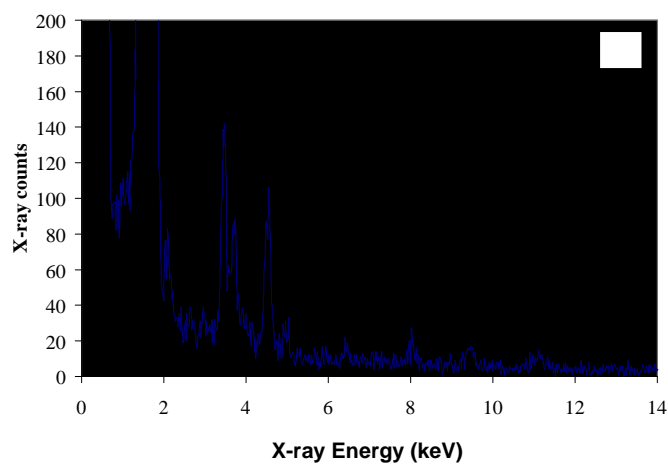
FIG. 1. Pt-Sn particles on MgO.

FIG. 2. Spectum from 3-nm Pt-Sn particle.
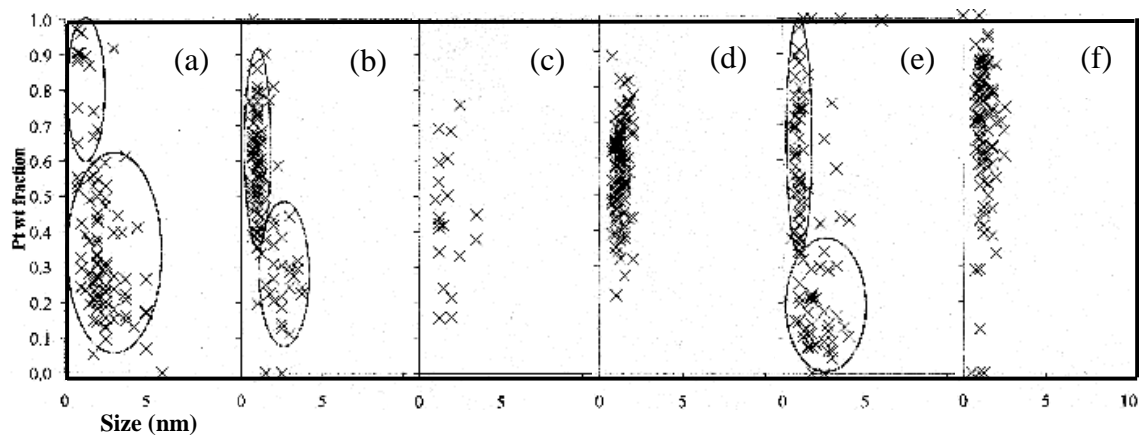

FIG. 3. Composition-size diagrams for fresh and reduced Pt-Sn nanoparticles on various support materials. (a) fresh Pt-Sn/γ-Al$_2$O$_3$, (b) reduced Pt-Sn/γ-Al$_2$O$_3$, (c) fresh Pt-Sn/MgO, (d) reduced Pt-Sn/MgO, (e) fresh Pt-Sn/modified hydrotalcite, (f) reduced Pt-Sn/modified hydrotalcite.