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Infrared Evidence for the Segregation of Silica-Supported Pt–Pd Bimetallic Clusters in Oxidizing Atmospheres

Gomez *et al.* (*1–3*), have reported that supported Pt–Pd catalysts prepared by the coimpregnation of alumina with $PdCl_2$ and $H_2PtCl_6 \cdot 6H_2O$ do not form bimetallic clusters. Sinfelt *et al.* (*4*) have shown quite convincingly that bimetallic clusters can form even in cases where alloy formation is not predicted on thermodynamic grounds. The results of Gomez *et al.* (*3*), however, seemed rather surprising to us in view of the phase diagram for Pt–Pd alloys which shows complete miscibility over the entire composition range. Recently, Chen and Schmidt (*5*) have shown that the oxidation of silica-supported Pt–Pd clusters followed by reduction in H_2 resulted in the formation of Pt and Pd-rich particles. Using infrared spectroscopy to study the chemisorption of CO on a silica-supported 1 : 1.1 Pt–Pd sample, we have obtained results which we believe are explained by the findings of Chen and Schmidt (*5*) and are not inconsistent with those of Gomez *et al.* (*3*).

The silica-supported bimetallic Pt–Pd samples used in this study were prepared by the coprecipitation of $H_2PtCl_6 \cdot 6\ H_2O$ (Strem Chem., Boston, MA) and $PdCl_2$ (Ventron Alpha Prod., Beverly, MA) onto a silica-support (Cab-O-Sil, Grade M-5, Cabot Corp., Boston, MA). The slurry was then air dried at room temperature for 1 week stirring regularly to retain uniformity. The dried catalyst was ground into a fine powder, less than 45 μm, and pressed into self-supporting disks 25 mm in diameter and having a thickness of 16 mg/cm². Metal dispersions as measured by H_2 gas adsorption were 18%. All spectra, with the exception of those shown in Fig. 2, were run at room temperature on a Perkin-Elmer Model 281 infrared spectrometer. The spectra shown in Fig. 2 were run at room temperature on a Perkin-Elmer Model 521 infrared spectrometer. Initial pretreatment was as follows: heated at 350°C in vacuum for 1 h followed by reduction in flowing H_2 at 350°C for 6 h. Subsequent standard reductions were for 4 h at 350°C. Oxygen pretreatments depended on the particular experiment and are specified in the text. The infrared cell and gas purification treatments are described elsewhere (*6*).

The stepwise adsorption and desorption of CO are shown in Fig. 1. The high-frequency infrared absorption band centered at 2085 cm^{-1} can be readily removed by evacuating the sample at room temperature and is assigned to CO linearly bound to Pd. The shoulder at 2075 cm^{-1} is assigned to CO linearly bound to Pt. This species is strongly adsorbed and cannot be removed by evacuation. The bands below 2000 cm^{-1} are assigned to CO multiply coordinated to Pd (*7*). The intensity of these bands relative to those of the linear Pd–CO bands are sharply decreased for the Pt–Pd bimetallic sample. This is readily explained if one considers that on silica-supported Pt, CO is only linearly adsorbed. When Pt–Pd bimetallic clusters are formed, the number of sites containing adjacent Pd atoms is decreased. Since these sites are necessary for bridging, less bridging can occur on the bimetallic samples and, therefore, the intensity of the bridged CO bands relative to the linear Pd–CO bands is decreased. Similar results have been observed by Soma-Noto and Sachtler (*8*) on a series of silica-supported Pd–Ag samples.

About 1 year prior to the publication of the paper by Chen and Schmidt (*5*), we obtained some rather puzzling spectra that we were at a loss to explain. During the stepwise adsorption of NO on a silica-supported Pt–Pd bimetallic sample, it be-

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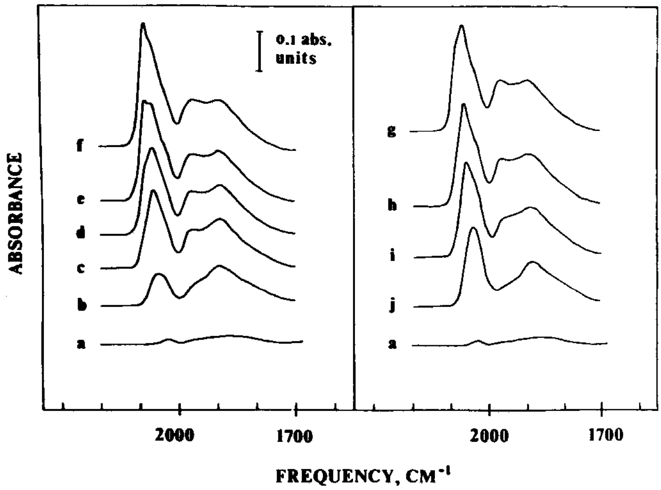

FIG. 1. Adsorption and desorption of CO on silica-supported 1 : 1.1 Pt–Pd bimetallic clusters: (a) background; (b) total CO pressure in cell = 5 × 10^{-3} Torr; (c) total CO pressure in cell = 9 × 10^{-2} Torr; (d) total pressure of CO in cell = 0.5 Torr; (e) total pressure of CO in cell = 3 Torr; (f) total pressure of CO in cell = 13 Torr; (g) evacuate 1 min CO pressure = 0.2 Torr; (h) evacuate 2 min CO pressure = 3 × 10^{-2} Torr; (i) evacuate 5 min CO pressure 3 × 10^{-3} Torr; (j) evacuate 3 h CO pressure <1 × 10^{-5} Torr.

came apparent from the infrared spectra that the NO was contaminated with O_2. At an NO pressure of 10 Torr, the infrared doublet characteristic of gas phase NO_2 was observed at 1625 and 1597 cm^{-1}. At this point, the experiment was stopped and the sample was subjected to a standard 4-h reduction at 350°C in flowing H_2. A stepwise adsorption of CO was performed and the results are shown in Fig. 2. There is a broadening of the linear CO bands and an increase in the intensity of the bridged CO bands relative to the linear CO bands. In light of the findings of Chen and Schmidt (5), we now believe that the surface of the Pt–Pd bimetallic cluster was oxidized by both O_2 and NO_2. After a subsequent reduction, Pt- and Pd-rich particles were formed. This resulted in an increase in the number of dual Pd sites necessary for the adsorption of bridging CO molecules.

Several other experiments were performed to verify these initial observations. Figure 3 shows the effect of displacing chemisorbed CO by NO on a supported Pt–Pd sample. Following the addition of 15 Torr of NO, all the CO was displaced with the exception of a species whose infrared absorption frequency was 2025 cm^{-1}. The sample was then evacuated to a pressure of 8 × 10^{-3} Torr and 11 Torr of CO was added. Initially, the intensity of all the bands was

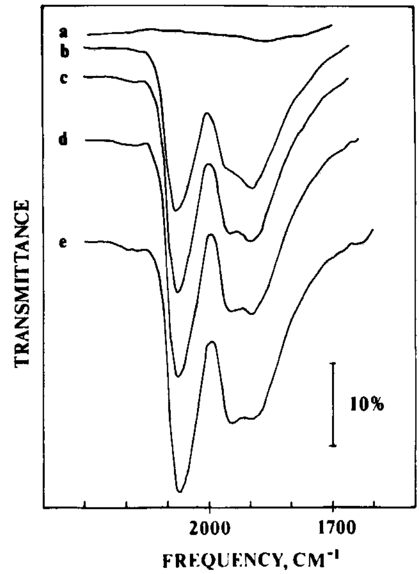

FIG. 2. Adsorption of CO on silica-supported 1 : 1 Pt–Pd bimetallic cluster after exposure to O_2 and NO_2: (a) background; (b) first addition of CO; (c) second addition of CO; (d) third addition of CO; (e) fourth addition of CO. Final pressure ≈15 Torr.

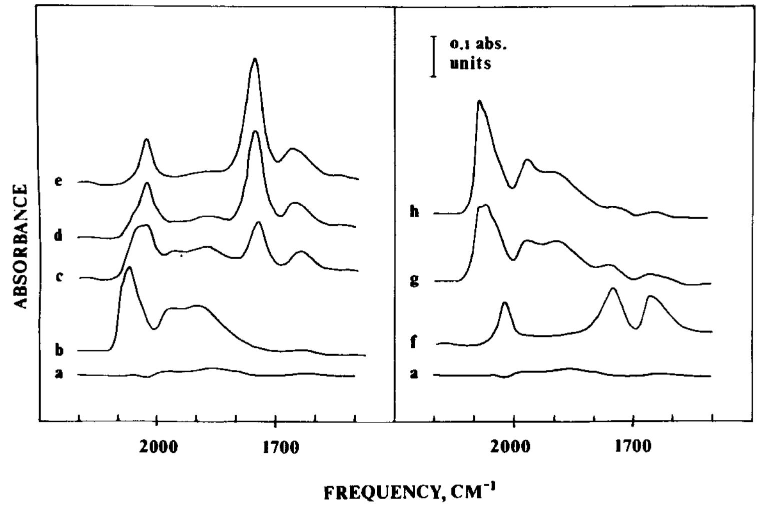

FIG. 3. Interaction of CO and NO on silica-supported 1 : 1.1 Pt–Pd bimetallic clusters: (a) background; (b) addition of 11 Torr CO to cell followed by 1 min evacuation. Final pressure = 0.2 Torr; (c) addition of 0.3 Torr NO to cell; (d) addition of 3 Torr NO to cell; (e) addition of 15 Torr NO to cell; (f) evacuate 6 min. Final pressure = 8×10^{-3} Torr; (g) addition of 11 Torr CO to cell; (h) after system was allowed to stand for 7 h.

depressed. On standing for several hours, the intensity of all the bands gradually increased. Of special interest was the increase in the intensity of the bands assigned to bridged CO relative to those of the linear Pd–CO band. We have shown in a previous report (*7*) that CO_2 and N_2O are formed when CO and NO are coadsorbed on supported Pd. Eischens and Pliskin (*9*) and Gonzalez and Brown (*10*) have shown that CO_2 is dissociatively adsorbed on supported Pt. This dissociative adsorption of CO_2 may result in the partial oxidation of the Pd surface. When CO is back-added, a slow reduction takes place resulting in the formation of Pd-rich and Pt-rich particles. A prerequisite for metal particle segregation in supported Pt–Pd bimetallics then appears to be oxidation followed by reduction.

Finally, we duplicated the experiments of Chen and Schmidt (*5*) with the exception of preparation techniques as closely as possible. Their samples were prepared by sequentially depositing Pt and Pd by vacuum evaporation onto amorphous silica while ours were prepared by coimpregnation techniques. Following the initial standard reduction, the sample was oxidized at 350°C in 1 atm of air for 10 min. The sample was then reduced in flowing H_2 at room temperature for 12 h. The results which are shown in Fig. 4 clearly show that the intensity of the bands assigned to bridging CO on Pd relative to those of linear Pd–CO in crease following the oxidation–reduction cycle. The cell was then evacuated and the sample oxidized once more in 500 Torr of air at 350°C for 15 min. When CO was adsorbed, the intensity of the bridged band again increased relative to the Pd–CO linear band.

The results reported here confirm those published by Chen and Schmidt (*5*) and explain the failure of Gomez *et al.* (*3*) to observe supported Pt–Pd bimetallic clusters. These authors pretreated their samples in air at 120°C prior to reduction. Folowing reduction, they characterized their samples using an oxygen–hydrogen titration technique which may have induced the metallic particle segregation that they observed. Pt–Pd clusters do form on silica; however, these clusters are highly unstable

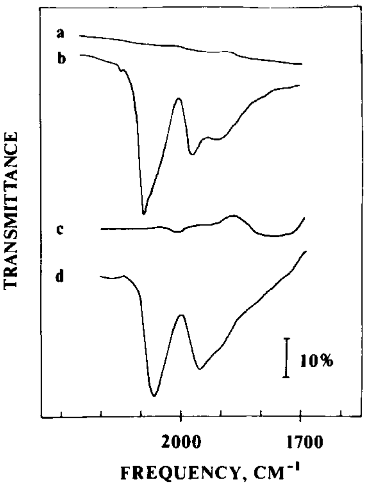

FIG. 4. Effect of oxidation on CO adsorption on silica-supported 1 : 1.1 Pt–Pd bimetallic clusters: (a) background for spectrum b; (b) standard 6-h reduction at 350°C followed by exposure to 1 atm of air at 350°C for 10 min. Sample then reduced in flowing H_2 at room temperature for 13 h. Addition of 19 Torr CO to cell; (c) background for spectrum d; (d) cell evacuated to 1 × 10^{-3} Torr, exposed to 500 Torr of air at 350°C for 15 min. Reduced in flowing H at room temperature for 10 h. Addition of 26 Torr of CO.

even in a mildly oxidizing atmosphere (i.e., $O_{2(g)}$ or $NO_{2(g)}$ at room temperature).

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