

INFRARED SPECTRA OF CARBON MONOXIDE CHEMISORBED ON SUPPORTED PLATINUM
AGGREGATES PREPARED FROM Pt CARBONYL CLUSTER COMPOUNDS

Masaru ICHIKAWA

Sagami Chemical Research Center, Nishi-Onuma, 4-4-1, Sagamihara, Kanagawa 229

Supported Pt aggregates have been prepared by pyrolysis of Pt₁₅-Pt₆ carbonyl cluster compounds highly dispersed on SiO₂ gel and γ-Al₂O₃, which showed the characteristic carbonyl ir spectra in CO chemisorption.

We have tried to prepare supported platinum aggregates¹⁾ by pyrolysis of the well-defined Pt carbonyl cluster anion salts highly dispersed on inorganic carriers such as silica and alumina surfaces. Such techniques provide arrays of discrete metal aggregates, the average diameter of which may be readily controlled down to below 15 Å.

The supported Pt aggregates (Pt₁₅-Pt₆) have been prepared by pyrolysis in vacuo (10⁻⁴ torr) of the trigonal prismatic Pt carbonyl cluster di-anion salts, $[\text{Pt}_3(\mu_2\text{-CO})_3(\text{CO})_3]_n[\text{N}(\text{C}_2\text{H}_5)_4]_2$ where n = 2-5, supported on silica gel and γ-Al₂O₃. Each Pt cluster anion salt was synthesized by carbonylation of PtCl₆²⁻ in NaOH-methanol solution and isolated as quaternary-ethylammonium salts after Chini et al.²⁾ The Pt carbonyl cluster anion salts were deposited in high dispersion (0.05-0.5 Pt wt %) from solutions of tetrahydrofuran and methanol onto γ-Al₂O₃ (Nishio-Kogyo Co. ; surface area 280 m²/g) and silica gel (Aerosil; surface area 300-380 m²/g), which were evacuated at 350°C for 20 hr prior to use. All the procedures were carried out under a vacuum or inert atmosphere of Ar and He due to the high air-sensitivity of the Pt carbonyl cluster anion salts. The desorption of CO from each dispersed Pt carbonyl cluster anion salt proceeded almost completely under a vacuum (10⁻⁴-10⁻⁵ torr) in the temperature range of 120-180°C, which was confirmed by temperature-programmed desorption techniques using mass spectrometry and gas chromatography with Active-carbon 2m column. Decomposition temperatures under He flow were 150°C for $[\text{Pt}_3(\mu_2\text{-CO})_3(\text{CO})_3]_5[\text{N}(\text{C}_2\text{H}_5)_4]_2$, 165°C for $[\text{Pt}_3(\mu_2\text{-CO})_3(\text{CO})_3]_3[\text{N}(\text{C}_2\text{H}_5)_4]_2$ and 170°C for $[\text{Pt}_3(\mu_2\text{-CO})_3(\text{CO})_3]_2[\text{N}(\text{C}_2\text{H}_5)_4]_2$, respectively, highly dispersed on γ-Al₂O₃.

The H_2 and CO adsorption isotherms were measured at $25^\circ C$, admitting the respective gases (50–250 torr) onto the resultant supported Pt aggregates. After measurement of the hydrogen adsorption isotherm, the sample was heated to $350^\circ C$ in flowing H_2 , held 2 hr and subsequently evacuated for 2 hr. After cooling to $25^\circ C$, CO adsorption was measured in a manner similar to that for hydrogen. A repetition of the pretreatment and H_2 and CO adsorption showed the sample to be unchanged throughout the H_2 and CO adsorption experiments. The amounts of H_2 and CO chemisorption were obtained by extrapolation of the linear portion above 150 torr to zero pressure. The ratios of the hydrogen chemisorbed to the total number of Pt atoms of supported Pt aggregates on $\gamma-Al_2O_3$ (in 0.2 Pt wt % dispersion), H/Pt , were measured to be 1.95, 1.7, 1.5 and 1.4 for Pt_{15} , Pt_{12} , Pt_9 and Pt_6 on $\gamma-Al_2O_3$, respectively. For CO adsorption, CO/Pt was determined to be 0.45, 0.37 and 0.25 over Pt_{15} , Pt_9 and Pt_6 on $\gamma-Al_2O_3$. Similar ratios (H/Pt and CO/Pt) in H_2 and CO adsorptions were obtained over the Pt aggregates deposited on silica gel, which were prepared from $[Pt_{15}(CO)_{30}][N(C_2H_5)_4]_2$ and $[Pt_9(CO)_{18}][N(C_2H_5)_4]_2$ in 0.5 Pt wt % dispersion.

The infrared spectra of the Pt carbonyl cluster anion salts dispersed on $\gamma-Al_2O_3$ and silica gel were measured before and after the heat-treatment in vacuo, and by introducing CO onto them. The sample wafers for infrared study were prepared by pressing about 100 mg of the supported Pt carbonyl cluster compounds on $\gamma-Al_2O_3$ or silica gel into a 2 cm diameter die under a force of 500 kg/cm^2 . The ir spectra were recorded in the region of 2500–1200 cm^{-1} using a Hitachi-EPI-G3 grating spectrophotometer.

The ir spectra of each Pt carbonyl cluster compound on $\gamma-Al_2O_3$ (1.8–2.0 Pt wt % dispersion) showed strong bands at 2040, 1850 cm^{-1} for $[Pt_{15}(CO)_{30}][N(C_2H_5)_4]_2$; 2025, 1830 cm^{-1} for $[Pt_{12}(CO)_{24}][N(C_2H_5)_4]_2$; 2005, 1810 cm^{-1} for $[Pt_9(CO)_{18}][N(C_2H_5)_4]_2$, and 1970, 1790 cm^{-1} for $[Pt_6(CO)_{12}][N(C_2H_5)_4]_2$, respectively, which are assigned³⁾ to the terminal and bridged carbonyl bands of the corresponding Pt carbonyl cluster compounds in solution and in crystal. Both carbonyl bands completely disappeared by evacuation of the sample wafers at 200–350 $^\circ C$ for 0.5 hr, probably due to desorption of CO from the dispersed Pt carbonyl clusters. After hydrogen treatment and evacuation of the samples at 350 $^\circ C$ for 0.5 hr, 5–250 torr of CO was admitted at 25 $^\circ C$ onto the resultant samples. The spectra

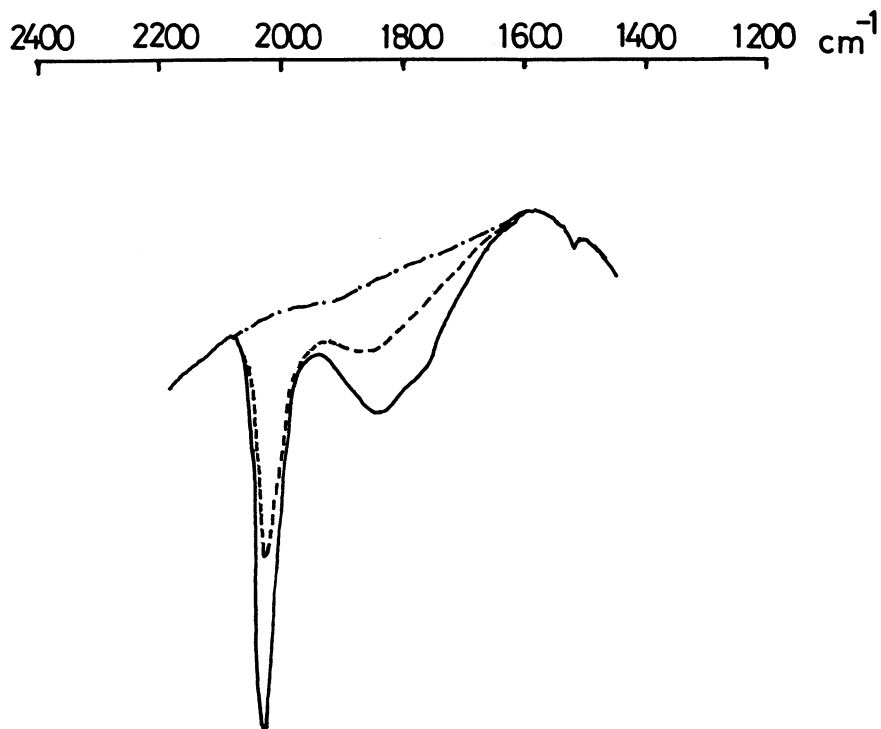


Figure 1a.

Infrared spectra of carbonyl of the $\text{Pt}_{15}(\text{CO})_{30}^{2-}\text{NEt}_4^+$ on $\gamma\text{-Al}_2\text{O}_3$ (1.2 Pt wt %) (———), after evacuation at 250°C in 0.5 hr (- - - - -) and of CO adsorbed on the resultant Pt aggregates: 100 torr of CO at 25°C (······).

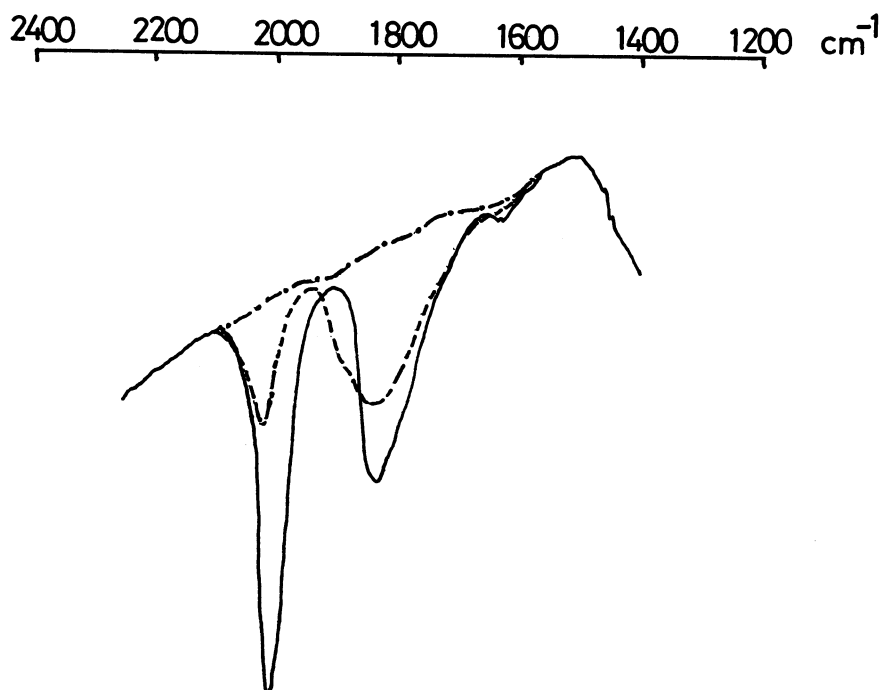


Figure 1b.

Infrared spectra of carbonyl of the $\text{Pt}_9(\text{CO})_{18}^{2-}\text{NEt}_4^+$ on $\gamma\text{-Al}_2\text{O}_3$ (1.6 Pt wt %) (———), after evacuation at 250°C in 0.5 hr (- - - - -) and of CO adsorbed on the resultant Pt aggregates: 100 torr of CO at 25°C (······).

results are recorded in Fig. 1a and 1b. By exposing the supported Pt_{15} on $\gamma\text{-Al}_2\text{O}_3$ to 100 torr of CO, a strong band at 2025 cm^{-1} and a medium intense band at 1820 cm^{-1} were observed as shown in Fig. 1a. For the Pt_9 sample, the ir spectra showed a weak band at 2000 cm^{-1} and intense band at $1805\text{-}1840\text{ cm}^{-1}$ in CO adsorption (Fig. 1b). In the C-O stretching region around 2000 cm^{-1} our results are similar to those of Eishens et al.⁴⁾ and other workers⁵⁾ in the appearance of the most intense band above 2020 cm^{-1} which assigned to terminal carbonyl band. The bands at the lower wave numbers around 1810 cm^{-1} , the appearance of which has been recently mentioned by Blyholder et al.⁶⁾ who used a highly dispersed sublimed Pt film, which may be due to CO chemisorbed on Pt atoms with relatively lower coordination numbers. It is of interest to note that both chemisorbed carbonyl bands are shifted to lower wave numbers ($30\text{-}40\text{ cm}^{-1}$) over the smaller Pt aggregates prepared from $\text{Pt}_{15}\text{-Pt}_6$ carbonyl clusters on $\gamma\text{-Al}_2\text{O}_3$, and the relative intensities of the bands around 1810 cm^{-1} increased (rather than those around 2000 cm^{-1}) for the smaller Pt aggregates. Instead of $\gamma\text{-Al}_2\text{O}_3$, a disk of dispersed $[\text{Pt}_{15}(\text{CO})_{30}]\text{N}(\text{C}_2\text{H}_5)_4)_2$ on silica gel (in 1.8 Pt wt % dispersion) was prepared and the ir spectra of the resultant sample after evacuation at 250°C for 1 hr showed CO bands at 2052 cm^{-1} (strong) and 1840 cm^{-1} (medium), similar to those of the Pt_{15} on $\gamma\text{-Al}_2\text{O}_3$, by admitting 100 torr of CO at 25°C . Subsequent exposure of the sample wafers to air at room temperature for 12 hr eliminated all the bands of the chemisorbed CO and CO_2 was detected in the gas phase.

Accordingly, the results suggest that the Pt aggregates prepared from the Pt carbonyl cluster compounds dispersed on $\gamma\text{-Al}_2\text{O}_3$ or silica gel contain the Pt atoms with the lower coordination numbers, which display the preferential appearance of the carbonyl ir bands around $1800\text{-}1840\text{ cm}^{-1}$ in CO adsorption.

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(Received December 24, 1975)