

Pt Particles from the $\text{Pt}_{15}(\text{CO})_{30}^{2-}$ Cluster Compound

B. E. HANDY,* J. A. DUMESIC,† AND S. H. LANGER

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

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Highly dispersed platinum particles were prepared by the pyrolysis of $\text{Pt}_{15}(\text{CO})_{30}^{2-}$ on hydroxylated and dehydroxylated, high surface area $\gamma\text{-Al}_2\text{O}_3$. Metal carbonyl decomposition was monitored by infrared spectroscopy, transmission electron microscopy, and hydrogen and carbon monoxide chemisorption experiments. The catalytic properties of these materials were examined for isomerization and hydrogenolysis of neopentane at 523–623 K and 1 atm pressure. The metal carbonyl cluster is weakly adsorbed on initial contact with the alumina surface showing CO stretching bands characteristic of the original cluster molecule. After several days of contact, or upon heating, the cluster rearranges to a more bulk-like platinum form. The original cluster compound cannot subsequently be regenerated with exposure to CO or mild reduction treatment. Metal particles originating from the Pt_{15} cluster are highly dispersed. Preliminary neopentane reaction studies show high selectivity for hydrogenolysis, following treatment in hydrogen at 620 K, consistent with the selectivity of highly dispersed platinum catalysts. Following reduction at 1070 K, the selectivity shifted to favor isomerization. Since electron microscopy results indicated minor particle sintering, the selectivity change may be attributed to surface annealing of the defect crystallite structures from the initial cluster at the higher reduction temperature. © 1990 Academic Press, Inc.

INTRODUCTION

The use of organometallic compounds as precursors for supported metal particles has been an active research area for the last 20 years (1–7). Both fundamental and practical considerations motivate using these compounds to prepare heterogeneous catalysts. For example, immobilization of a cluster compound on an inorganic oxide support material followed by ligand removal may provide a well-defined particle structure related to the metal framework of the precursor compound. Analysis of the kinetics of reactions occurring over such particles can lead to enhanced understanding of the nature of the active sites. In addition, cluster compound decomposition on supports might produce supported metal catalysts

with properties related to the choice of precursor molecule or the decomposition regimen. Further opportunities exist when two or more different metals (1, 2, 7) are involved. The decomposition of multimetallic clusters represents a direct path to controlling metal composition and the degree of metal–metal association in multimetallic catalysts. The existence of highly dispersed bimetallic particles, with metal ratios that are unattainable in a bulk phase, has been reported by Sinfelt and others (8–10).

Investigations of large Pt clusters as precursors for supported metal particles have involved studies of catalysts prepared from Pt_3 through Pt_{15} dianions. Ichikawa (11, 12) decomposed $[\text{Pt}_n(\text{CO})_6]_n^{2-}$ ($n = 2-5$) on $\gamma\text{-Al}_2\text{O}_3$ and silica gel that had been previously dehydrated in vacuo at 612 K. The decarbonylation process occurred in the temperature range of 393–453 K. The infrared spectra of the freshly prepared samples showed carbonyl bands characteristic of the precursor molecule which disappeared after evac-

*Present address: Dept. Industrial and Engineering Chemistry, Eidgenössische Technische Hochschule (ETH)-Zentrum, CH-8092 Zürich, Switzerland.

†To whom correspondence should be addressed.

uation at 512 K but were reinstated after reduction at 612 K, evacuation, and exposure to 100 Torr of CO at room temperature. Subsequent exposure to air at room temperature eliminated CO bands while CO₂ was detected in the gas phase. Hydrogen and CO chemisorption isotherms obtained following reduction and evacuation at 612 K established that the platinum dispersion was very high; e.g., H/Pt and CO/Pt values on Pt₁₅-derived catalyst were 1.95 and 0.45, respectively. The high intensity of the μ_2 -CO IR absorption band (bridge-bonded CO) indicated the presence of Pt sites not normally seen on bulk Pt particles. Catalysts derived from the smaller Pt₃-Pt₆ clusters exhibited higher hydrocracking and cyclization selectivity than the larger precursors, suggesting that these clusters had a larger number of low-coordination sites. Garin *et al.* (13) found similar selectivity patterns for cluster-derived and conventionally derived catalysts, although the cluster catalysts were less active but more stable to coke deactivation. The faster demethylation of methycyclopentane than ring-opening with Chatt clusters (Pt₃(μ_2 -CO)₃L₄; L = PPh₃ or PEt₃) as precursors was attributed to cyclization sites blocking from phosphorous contamination. This selectivity difference disappeared with catalyst treatment in air at 473 K to remove the phosphorous. The activity of Pt-Sn catalysts derived from [PtCl₂(SnCl₃)₂]²⁻ or [Pt₃(SnCl₃)₂](C₈H₁₂)₃ complexes was lower than that of conventional Pt catalysts (14). Low reforming activity suggested intimate association of the two metals with Sn poisoning the Pt sites.

The present study deals with the characterization of catalysts prepared from Pt₁₅(CO)₃₀²⁻ decomposition on γ -Al₂O₃. In addition to infrared studies of the decomposition process, structural and elemental information on supported Pt particles was obtained with transmission electron microscopy. These latter investigations were supplemented with studies of metal carbonyl decomposition on thin alumina films, since such supports allow high quality

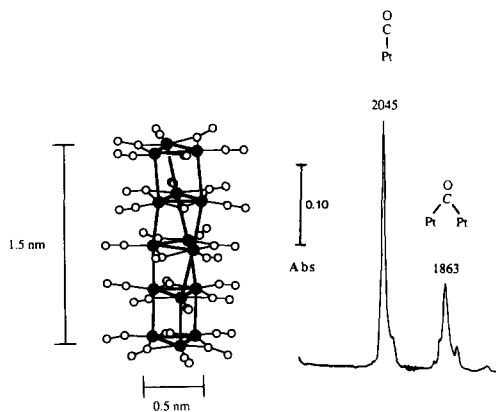


FIG. 1. Molecular structure of Pt₁₅(CO)₃₀²⁻ and the corresponding infrared spectrum of the CO-stretching region. Figure adapted from Chini (26).

electron micrographs to be obtained. The metal dispersions of high surface area catalysts were measured by selective chemisorption. Finally, the catalytic properties of the supported Pt materials were probed by studying structure-sensitive neopentane isomerization/hydrogenolysis reactions.

EXPERIMENTAL

The Pt₁₅ cluster compound employed in this study was synthesized by Dr. R. Nagaki in the research group of Professor L. F. Dahl (Department of Chemistry, University of Wisconsin, Madison) using a previously published method (15). Crystals of the methyltriphenylphosphonium salt, [Pt₁₅(CO)₃₀][MePPh₃]₂ were used in catalyst preparation. The Pt₁₅(CO)₃₀²⁻ molecule (16) consists of five elements of the subunit Pt₃(μ_2 -CO)₃(CO)₃, as depicted in Fig. 1. Within each subunit, three carbonyl ligands, designated μ_2 -CO, are bridge-bonded across two metal atoms, and three are terminally (t) bonded to each metal atom. The CO stretching frequencies correspond closely to the values published by Calabrese *et al.* (16). Although both t-CO and μ_2 -CO ligands are in equal numbers on the molecule, the μ_2 -CO band, centered at 1863 cm⁻¹, is about $\frac{1}{3}$ as intense as the t-CO band, centered at 2045 cm⁻¹.

The support material used in the preparation of high surface area catalysts was ALON C (Degussa), a gamma-phase aluminum oxide with a BET area of $100 \text{ m}^2/\text{g}$. Before use, the support was calcined for at least 6 h at 870 K in flowing oxygen. Following calcination, the support was used either in a partially dehydroxylated state (PDA) or further dehydroxylated by heating under argon to 1220 K for 1 h (DA). This nomenclature is similar to that of Burwell (17). The degree of dehydroxylation was monitored in the $3500\text{--}4000 \text{ cm}^{-1}$ IR region. Metal carbonyl cluster-derived catalysts were prepared by slurrying support powder with a solution of THF containing the Pt_{15} cluster compound. During the earlier portion of experimental work, the preparation and handling of cluster-derived catalysts was performed in a glove bag (Atmosbag, Aldrich Chemicals, Inc.) using purified argon. The chemical impregnation was complete after 1 to 3 days, as evidenced by the change in color of the solution from green to light brown and of the support from white to a light grayish color. The slurry was filtered on a glass frit located in a side arm of the flask and the sample was evaporated to dryness under a steady flow of argon. Phosphorous contamination stemming from the cation of the precursor salt was found to be below 10 ppm for a cluster catalyst containing 3 wt% Pt.

In the subsequent infrared analysis of the above samples, moisture contamination was evident. Accordingly, catalysts were also prepared in a glove box (Vacuum Atmospheres, Inc.), where oxygen and water contaminant levels were kept below 1 ppm. Infrared analysis showed that strong Pt-CO bands were present in fresh samples prepared in the glove box environment, whereas these bands were nearly absent from fresh samples prepared in the glove bag. This observation demonstrates the importance of maintaining a rigorously inert atmosphere to prevent the CO ligand loss, due to air and moisture sensitivity of these catalysts. Catalysts prepared with hydrox-

ylated, partially hydroxylated support, or dehydroxylated support exposed to ambient air, slowly turned dark green in color. However, all catalysts became gray-colored with thermal treatment above 400 K.

Infrared spectroscopy studies were conducted using a Nicolet Instruments Model 7199 Fourier transform infrared spectrometer with an MCT detector. Transmission spectra were obtained at 2 cm^{-1} resolution. Generally, 200 scans of the sample spectrum were collected and ratioed with 100 scans of the "background," which consisted of the calcium fluoride windows of the cell with treatment gases in the sample space. Sample wafers 1 cm in diameter were made from approximately 30 mg of catalyst powder. The wafers were pressed between two polished faces in a hand-driven pellet press (Foxoboro, Inc.). A 1-cm-o.d. stainless steel ring was inserted with the powder to provide mechanical stability to the fragile wafer.

Some infrared studies were conducted on catalyst specimens prepared by pretreating support wafers in an *in situ* cell. The cell is more thoroughly described in (18). The cell could be fully evacuated and the sample region heated to 1020 K. Gas flow rates typically used were 150–200 ml/min. Thermocouple location insured close correspondence between measured and true specimen temperatures. *In situ* runs consisted of mounting pure support wafers and precalcining them under helium flow. The cell was then removed to a glove bag and briefly opened to wet the specimen with several drops of cluster solution. The apparatus was then reinstalled in the spectrometer. Specimens were then heated at a rate of 20 K/min in flowing helium ($150\text{--}200 \text{ cm}^3/\text{min}$), with metal decarbonylation monitored continuously. This form of cluster deposition on support surface, termed "*in situ* impregnation" in the experimental results, gives a less uniform metal loading on the wafer while allowing less time for chemical fixation than the slurry method. Nevertheless, it sheds light on the decomposition behavior

of weakly adsorbed platinum cluster carbonyl on the support. Since infrared spectral collection required about 30 s, the temperature resolution of each spectrum obtained during the heating process was 10 K. Some spectra were taken at isothermal conditions. Unless otherwise specified, sample spectra were ratioed against the empty cell background spectrum under helium flow. No correction was made for temperature. A second cell (19) was also used for infrared studies, containing a quartz section for thermal treatment and an unheated end equipped with CaF_2 windows. The sample was fastened to a stainless steel mount that could be slid to either end for treatment or IR analysis. The catalyst wafer was loaded into this cell in a glove box. In a typical procedure, the sample was treated for 30-min periods at fixed temperatures, after which the cell was cooled to room temperature and inverted to slide the specimen mount to the window section. The mount could be stopped short of the window so that a background spectrum could be obtained of windows and gas.

The batch recycle reactor and analytical methods used for neopentane conversion studies have been described elsewhere (18). The platinum loadings of all high surface area catalysts were determined by Galbraith Laboratories, Inc.

RESULTS

Infrared Spectroscopy

Catalysts prepared by in situ impregnation. Although the support wafers were dehydroxylated at 1220 K prior to wetting with solution, rehydroxylation occurred either from exposure to residual moisture in the glove bag or possibly THF solvent cracking on the dry alumina surface. Specifically, a weak IR peak at 1640 cm^{-1} , which corresponds to a water bending mode, indicated the presence of physisorbed water. Furthermore, the hydroxyl stretching region ($3500\text{--}4000\text{ cm}^{-1}$) resembled the spectrum of a hydrated support dried at 373 K, with a small amount of physisorbed water present. Two peaks, at 3672 cm^{-1} and 3702 cm^{-1} ,

appeared on the high-frequency shoulder of the broad hydrogen-bonding band. Other isolated OH group peaks appeared during heating. Thus, the decomposition behavior observed represents decarbonylation behavior on a hydroxylated alumina (HA) surface.

Infrared spectra of the CO stretching region are presented in Fig. 2. Immediately after the support was wetted with the cluster solution, the narrow CO bands characteristic of the solvated cluster molecule became apparent (spectrum 1). With drying under helium flow, the bands broadened and shifted slightly upward in frequency (spectrum 2). This blue-shift could represent oxidation of the cluster molecule, by association with a surface hydroxyl group. The room temperature spectrum (spectrum 3) was stable for several hours, and showed peaks at 2058 cm^{-1} and 1862 cm^{-1} , corresponding to the linearly bonded (t-CO) and bridge-bonded ($\mu_2\text{-CO}$) ligands, respectively. The $\mu_2\text{-CO}$ peak is $\frac{1}{3}$ as intense as the t-CO peak, suggesting a fully carbonylated cluster molecule. The bands did not change in strength or position during heating under flowing helium until 333 K, when both bands simultaneously weakened and shifted toward lower frequencies (spectrum 4). At 343 K, the t-CO peak was centered at 2038 cm^{-1} and the $\mu_2\text{-CO}$ peak was at 1810 cm^{-1} (spectrum 5). In some experiments, both the original and new t-CO peaks were present, with the new peak strengthening at the expense of the original peak. The $\mu_2\text{-CO}$ peak weakened in parallel with the original t-CO peak disappearance. The new t-CO peak position is similar to that from CO adsorbed on Pt particles at saturation coverage. Weakening and red-shifting of the new t-CO band was seen with increasing temperature, also characteristic of CO adsorbed on Pt particles, due to diminished dipole-dipole coupling with decreasing CO coverage. These results suggest Pt_{15} cluster rearrangement to bulk-like form near 340 K, with residual CO ligands assuming the behavior of CO adsorbed on Pt.

The possibility of cluster regeneration by

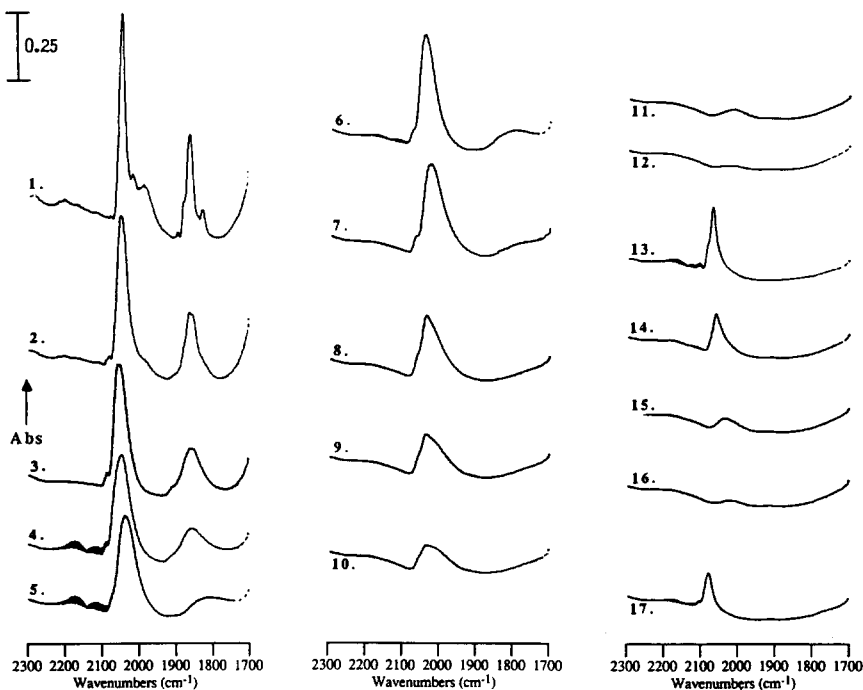


FIG. 2. Infrared spectra of $\text{Pt}_{15}/\text{DA}^*$ prepared by *in situ* impregnation, following successive treatments. (1) freshly wetted, (2) after 1 min He flow, (3) after 30 min He flow, (4) 333 K under He with residual CO, (5) 343 K under He with residual CO, (6) exposed to 100 kPa CO, cooled to 298 K, (7) 373 K under He flow, (8) 433 K under He flow, (9) 453 K under He flow, (10) 473 K under He flow, (11) 512 K under He flow, (12) 573 K under He flow, (13) exposed to 100 kPa CO at 298 K, (14) 473 K under He flow, (15) 523 K under He flow, (16) 573 K under He flow, (17) exposed to residual CO at 298 K.

reexposure to CO gas was explored at the initial point of decarbonylation (340 K) by switching the gas flow to pure CO at 1 atm, then cooling to room temperature and purging the cell with helium. While the μ_2 -CO peak was not regenerated (spectrum 6), the t-CO peak was strengthened. The gas flow was then switched to helium, and heating continued to 593 K. The remaining μ_2 -CO peak disappeared at 412 K. The t-CO peak weakened and broadened at 433 K, as seen in spectrum 8. This peak was not completely removed until 573 K (spectrum 12), at a frequency of 2017 cm^{-1} . Upon completion of the first decarbonylation cycle, the sample was cooled to room temperature and the gas flow switched to pure CO to produce a t-CO peak centered at 2072 cm^{-1} (spectrum 13). In addition to being at a higher frequency than the initial t-CO band, the regenerated

peak was narrower and about 40% less intense. No bands were present at the μ_2 -CO position. A medium-intensity band at 1599 cm^{-1} and a weak band at 1393 cm^{-1} also appeared upon CO exposure. These may be assigned to the asymmetric and symmetric stretch bands of metal formate or carboxylate species (20). Heating under helium to 573 K caused the t-CO peak to weaken and shift to lower frequency (spectra 14–16), behavior characteristic of CO on bulk-like platinum particles. The $1300\text{--}1700\text{ cm}^{-1}$ bands remain unchanged throughout the heating. The sample was cooled again to room temperature whereupon a final exposure to CO restored the t-CO peak, now centered at 2080 cm^{-1} , with an intensity of 25% of that observed initially. The progressive weakening of the t-CO band with each decarbonylation cycle is linked with in-

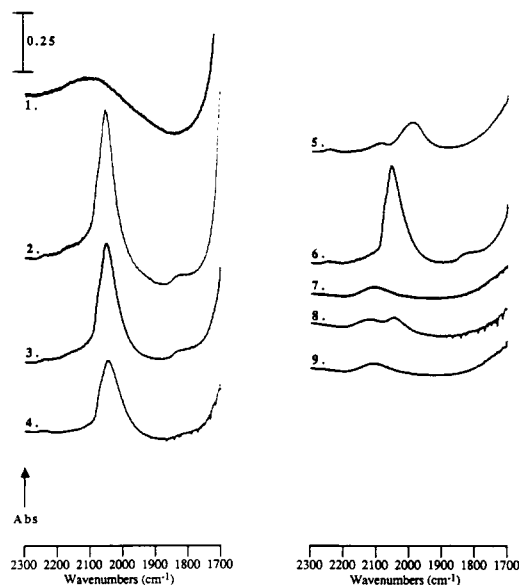


FIG. 3. Infrared spectra of Pt_{15}/PDA^* prepared by slurry method, following successive treatments. (1) freshly prepared, (2) exposed to 20 kPa CO at 298 K, (3) evacuated at 298 K, (4) evacuated at 373 K, (5) evacuated at 513 K, (6) exposed to 20 kPa CO at 298 K, (7) evacuated at 673 K, (8) exposed to 20 kPa CO at 298 K, (9) evacuated at 723 K.

creasing frequency, perhaps indicating a gradual oxidation of the platinum surface, and fewer sites accessible to CO. Tests with slurried catalyst samples below demonstrate that hydrogen reduction restores chemisorption capacity.

Slurried catalysts. Infrared spectra of catalysts prepared from slurrying cluster solution with support (PDA and DA alumina, as described earlier) were collected. These samples showed air/moisture sensitivity, since exposure to these contaminants showed carbonyl ligand loss greater than that for samples prepared and handled under more rigorously inert conditions. A series of spectra for Pt_{15}/PDA^* , where the asterisk denotes that some air/moisture exposure had occurred during transfer to infrared cell, are shown in Fig. 3. Before treatment, the sample at room temperature under argon contained only one weak peak, centered at 2100 cm^{-1} (spectrum 1). Carbon monoxide at 20 kPa was then admitted and allowed to

equilibrate with the sample for 1 h. This produced a strong band corresponding to linearly bonded CO (t-CO) and a weak band due to bridge-bonded (μ_2 -CO) CO at 2055 cm^{-1} and 1833 cm^{-1} , respectively (spectrum 2). Evacuation at room temperature slightly weakened the bands (spectrum 3). Heating at progressively higher temperatures *in vacuo* both diminished and shifted the peaks. At 373 K, the t-CO peak had shifted to 2046 cm^{-1} , and the 1833 cm^{-1} μ_2 -CO peak had disappeared (spectrum 4). Upon heating to 513 K, the t-CO band weakened further and was shifted to 1991 cm^{-1} (spectrum 5). In addition, a smaller peak was present at 2088 cm^{-1} . Reexposure to CO restored the linear and bridged carbonyl bands and produced bands at 2056 cm^{-1} and 1834 cm^{-1} (spectrum 6). After heating to 673 K under vacuum, a single peak remained, centered at 2107 cm^{-1} (spectrum 7). The sample was exposed to CO once more to produce two weak peaks centered at 2120 cm^{-1} and 2044 cm^{-1} (spectrum 8). Finally, upon evacuation at 723 K, only a single CO peak at 2112 cm^{-1} remained (spectrum 9).

Evidence for isolated hydroxyl groups began to appear on Pt_{15}/DA^* and Pt_{15}/PDA^* for treatments above 573 K. Peak locations for these groups were at 3782, 3717, 3669, and 3601 cm^{-1} . Peaks at 2962, 2926, and 2859 cm^{-1} appeared in all spectra, and became increasingly prominent with increasing treatment temperature. These peaks may be attributed to symmetrical and asymmetrical stretching modes of CH_3 and CH_2 groups, which can originate from the solvent or species from solvent decomposition on the support.

In the absence of air or moisture, the Pt carbonyl cluster on alumina was more stable. Catalyst $Pt_{15}(-Sn)/DA$ was prepared by the slurry method in the inert atmosphere of a glove box. The tin label in this catalyst designation indicates a small amount of tin in the impregnating solution but an amount not large enough to affect appreciably the cluster behavior (Pt:Sn = 40). Infrared spectra for thermal decomposition of this

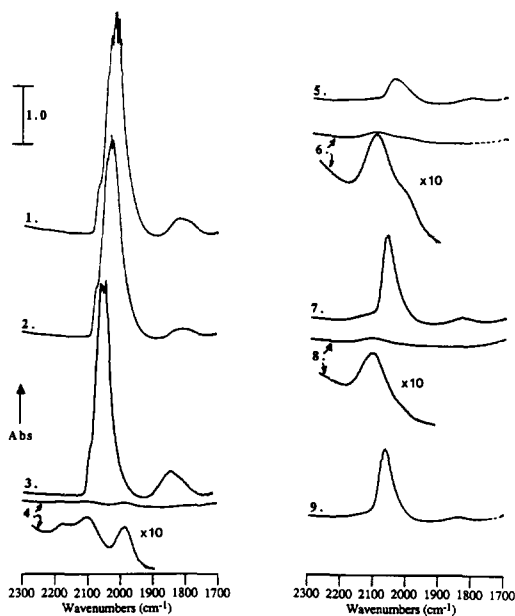


FIG. 4. Infrared spectra of $\text{Pt}_{15}(-\text{Sn})/\text{DA}$ prepared by slurry method, following successive treatments. (1) freshly prepared, (2) heated to 373 K in He, (3) in 25 kPa CO at 298 K, (4) heated to 512 K in He, (5) in 20 kPa CO at 298 K, (6) reduced in H_2 at 573 K, (7) in 25 kPa CO at 298 K, (8) reduced in H_2 at 623 K, (9) in 25 kPa CO at 298 K.

catalyst are shown in Fig. 4. The spectrum of freshly dried catalyst (spectrum 1) contained a broad t-CO peak, centered at 2026 cm^{-1} , and a medium-intensity μ_2 -CO peak at 1820 cm^{-1} . Heating in flowing helium to 370 K slightly weakened and shifted the μ_2 -CO band to 1805 cm^{-1} ; however, additional exposure to CO intensified both bands, and enhanced the μ_2 -CO band beyond its initial intensity (spectrum 3). With heating in helium to 512 K, there was considerable band weakening and transformation to three weak bands, centered at 2168, 2100, and 1983 cm^{-1} (spectrum 4). The 1983 cm^{-1} peak was the strongest of the three, and may be interpreted as a t-CO band from bulk-like Pt particles, red-shifted because of reduced dipole-dipole coupling. The higher frequency bands suggest t-CO coordinated to oxidized platinum. Reexposure to CO restored the t-CO peak at 2047 cm^{-1} and the

weak μ_2 -CO peak at 1812 cm^{-1} (spectrum 5), although these peaks were weaker than in the fresh sample. The t-CO/ μ_2 -CO intensity ratio was about 5 : 1. The band positions are consistent with conventional platinum particles, although higher t-CO/ μ_2 -CO intensity ratios are normally expected (21). Thus, the cluster-derived particles at this stage seemed to retain an enhanced capacity for bridge-bonded CO ligands.

The spectrum after reduction in hydrogen at 573 K indicated that CO was not completely desorbed, remaining as a weak band centered at 2105 cm^{-1} and a shoulder at 2022 cm^{-1} (spectrum 6). This reduction treatment restored about half of the original adsorption capacity of Pt (compare 7 to 1), evidenced by the appearance of t-CO and μ_2 -CO bands upon exposure to CO. Importantly, the t-CO/ μ_2 -CO intensity ratio had increased, approaching characteristics of conventionally prepared platinum particles. The sample was then reduced at 623 K, where only a weak band at 2111 cm^{-1} was present (spectrum 8). The final reexposure to CO partially restored the intensity of the t-CO peak at 2068 cm^{-1} , with a weak μ_2 -CO peak at 1833 cm^{-1} (spectrum 9). The t-CO/ μ_2 -CO ratio was then 22 : 1.

Hydrogen and CO chemisorption on cluster-derived catalysts.

Chemisorption results on the Pt_{15} -derived catalysts were consistent with an irreversible rearrangement of the Pt_{15} cluster into highly dispersed Pt particles. Untreated samples that were evacuated at room temperature showed subsequent high CO adsorption, although the amounts were not sufficient to regenerate the $\text{Pt}_{15}(\text{CO})_{30}^{2-}$ precursor. This result is consistent with the infrared spectra, which contained a strong t-CO band and a weaker μ_2 -CO band. In the untreated, air-contaminated $\text{Pt}_{15}/\text{PDA}^*$ catalyst (Table 1), CO uptake amounted to $\text{CO}/\text{Pt} = 0.52$, whereas this ratio decreased to 0.26 for the catalyst maintained under inert conditions (Table 1). The difference in CO chemisorption capacity can be explained by

TABLE I
Chemisorption Results for Alumina-Supported Pt Catalysts Following Successive Treatments

Catalyst	Metal loading (wt%)	Treatment	H/Pt	CO/Pt
Pt ₁₅ /PDA*	0.35% Pt	Evacuated at 298 K		0.52
		Evacuated at 523 K		0.30
		Reduced in H ₂ at 623 K	0.41	
		Evacuated at 623 K		0.40
Pt ₁₅ /DA	1.59% Pt	Reduced in H ₂ at 623 K	0.40	
		Evacuated at 623 K		0.45
Pt ₁₅ (-Sn)/DA	1.45% Pt 0.04% Sn	Evacuated at 523 K		0.26
		Reduced in H ₂ at 623 K	0.27	
		Evacuated at 623 K		0.36

more extensive carbonyl ligand loss in the air-contaminated catalyst. Following exposure to CO at room temperature, the Pt₁₅/PDA* sample was evacuated at 523 K and subsequently exposed to CO again at room temperature. The CO/Pt ratio decreased to 0.30 (see Table I), consistent with the IR spectra showing that all of the CO is not desorbed by 523 K. Hydrogen reduction of the sample at 623 K increases the CO uptake, giving a CO/Pt ratio of 0.40. The hydrogen adsorption capacity of the sample gives a H/Pt ratio equal to 0.41 after this treatment. Accordingly, the H/CO adsorption ratio is essentially equal to unity, a value characteristic of highly dispersed platinum particles.

The chemisorption results for the Pt₁₅/DA sample show values of the CO/Pt and H/Pt ratios equal to 0.45 and 0.40, respectively, following reduction in hydrogen at 623 K. These values, and the H/CO ratio equal to 0.9, all confirm the high dispersion of Pt on this sample. The results for the Pt₁₅(-Sn)/DA sample show values of the CO/Pt and H/Pt ratios equal to 0.36 and 0.27, respectively, following reduction in hydrogen at 623 K. These values, and the H/CO ratio, are slightly lower than for the above Pt₁₅/PDA* and Pt₁₅/DA samples. Thus, it appears that the Pt particles in the Pt₁₅(-Sn)/DA sample are not as highly dispersed, possibly a consequence of the Sn trace present.

The results of infrared and volumetric uptake studies of the Pt₁₅/PDA*, Pt₁₅/DA and Pt₁₅(-Sn)/DA show that highly dispersed platinum aggregates are formed from the Pt₁₅(CO)₃₀⁻ cluster molecule. The catalysts must be reduced at 623 K for complete decarbonylation of metal clusters and restoration of high chemisorption capacity.

Electron Microscopy

Freshly wetted, thin-film specimens showed evidence that cluster-sized platinum features were present (see Fig. 5). Examination at high magnification reveals an abundance of discrete, nanometer and subnanometer-sized platinum features. The annular dark field image (not shown) confirmed the presence of high atomic number atoms, i.e., light features for each platinum cluster against a dark background. The image contrast of subnanometer-sized features is derived mostly from phase contrast, rather than Bragg scattering (22), and the apparent particle size and contrast are dependent upon defocus. If the contrast level is proportional to the number of heavy atoms present, then the weakest features may be 15-atom Pt clusters, perhaps in the intact or related configuration of the metal framework of the precursor molecule. The darker features may be the result of molecular condensation of two or more 15-atom clusters, in the same

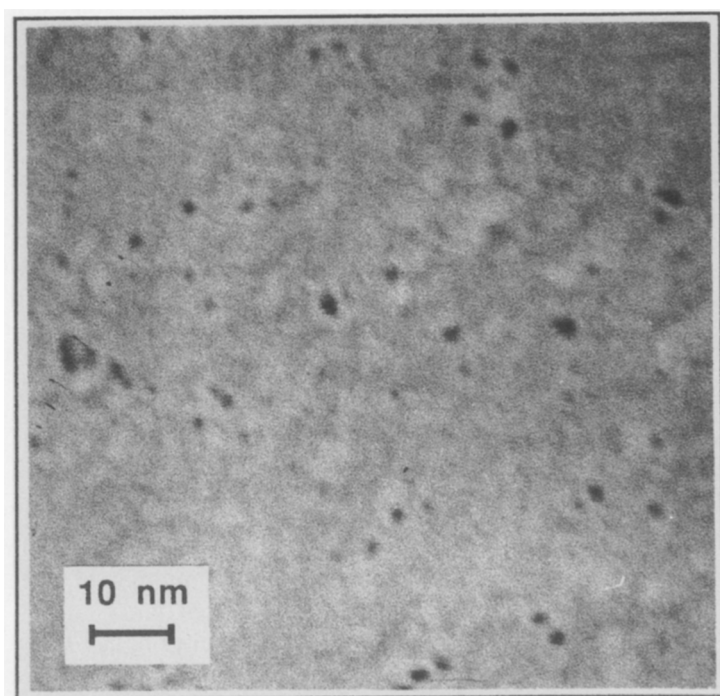
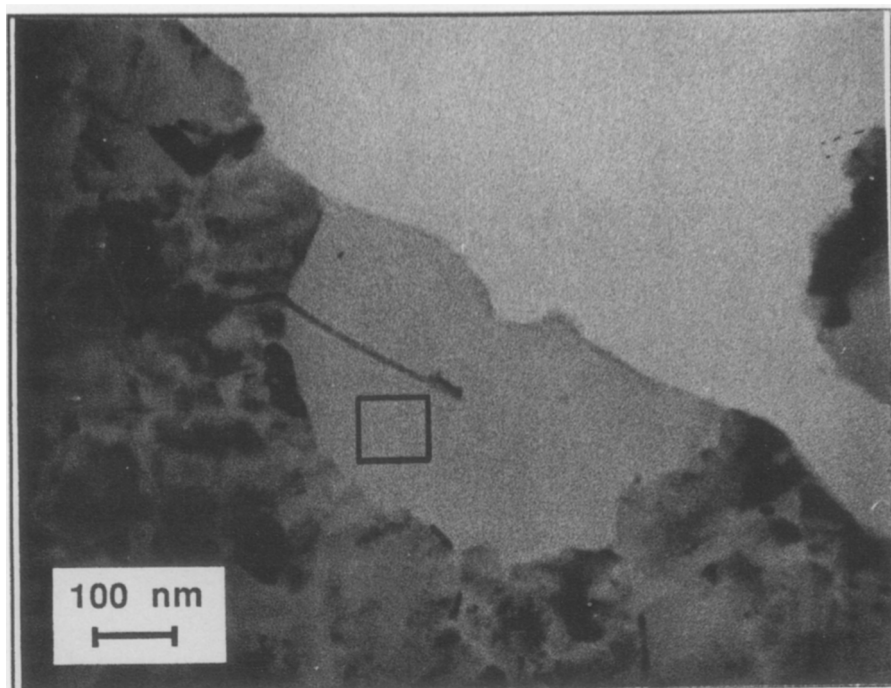


FIG. 5. Micrograph of a thin film specimen wetted with $\text{Pt}_{15}(\text{CO})_{30}^{2-}$ cluster solution. Enlarged area shows cluster-sized platinum features.

manner by which it has been explained (23) that the larger platinum cluster carbonyls are synthesized from smaller Pt cluster carbonyl subunits. The condensation process can be described as the progressive oxidation of the small anionic Pt clusters toward larger, zero-valent clusters. On the support, an oxidation environment exists in the form of alumina surface hydroxyl groups, which may interact with the Pt carbonyl molecules upon solution contact. The cluster sizes did not appear to be affected by exposure to the electron beam or to the room atmosphere.

A thin film specimen was successively analyzed following heating alternately in hydrogen and oxygen to a temperature of 513 K, followed by heating to 770 K. Particle growth was more strongly influenced by treatment temperature than by heating in an oxygen or hydrogen environment. Particles grew at 513 K to a size of about 1.5–2 nm by coalescence of nearest neighbors into larger platinum particles. Particle growth was extensive at 770 K, with the majority of the Pt particles in the size range from 3 to 10 nm.

High surface area, cluster-derived Pt/ Al_2O_3 catalysts were also analyzed by electron microscopy. Platinum particle sizes in a 3.28 wt% Pt sample of $\text{Pt}_{15}/\text{PDA}^*$, analyzed after 523 K reduction, were in agreement with the dispersion results from hydrogen chemisorption. In the platinum cluster catalysts $\text{Pt}_{15}/\text{DA}^*$ and $\text{Pt}_{15}/\text{PDA}^*$, characterized by infrared and selective chemisorption, no metallic features larger than 2 nm were visible. The cluster-derived catalysts $\text{Pt}_{15}(-\text{Sn})/\text{DA}$ and Pt_{15}/DA were analyzed by STEM following their use in neopentane conversion (as described below). Both catalysts had been subjected to two reaction runs, the first of which involved catalyst reduction at 623 K, and the second of which involved higher temperature reduction, i.e., 2 h at 870 K for $\text{Pt}_{15}(-\text{Sn})/\text{Da}$, 2 h at 1023 K for Pt_{15}/DA . The TEM results indicated that, despite the severe reduction treatments, the platinum was still highly dispersed, with an average particle size of between 2.0 and 3.0 nm. Very few particles

larger than 10 nm in size were observed. As discussed below, the reaction results show an increase in isomerization selectivity with increased reduction temperature, as expected for large particles. On the other hand, the overall activity level suggests a high Pt surface area. The amount of tin incorporated into the $\text{Pt}_{15}(-\text{Sn})/\text{DA}$ catalyst was small (0.04 wt%) and did not seem to modify platinum behavior in either reaction or infrared studies. Energy-dispersive X-ray analysis of the sample showed that the tin count level was always within range of the background noise level, in both blank areas and on platinum particles. Thus, the tin must be thinly dispersed over the support, and in such a state cannot be present in a sufficient concentration level near platinum particles to modify the metal function of the catalyst.

Results of neopentane conversion over several conventional and cluster-derived Pt catalysts are summarized in Table 2.

DISCUSSION

The two primary stages involved in the activation of catalysts prepared from organometallic compounds should be (i) immobilization of metal carbonyl cluster on the support surface, and (ii) decarbonylation to metal particles. In the first stage, the molecule should associate with surface groups, e.g., hydroxyl groups or Lewis acid-base pairs. In the second stage, assuming metal carbonyl stabilization at room temperature, thermal treatment is necessary for excess ligand removal to expose metal atoms. Thermodynamically, the stability of the metal carbonyl cluster is related to the strength of the metal–metal bonds and metal–ligand bonds. Since the latter have higher bond energies, most of the molecular stability is derived from the ligand coordination if there are an equal number of both bond types. Thus, although metal atoms must be exposed for catalysis, it may be necessary to form some bonds with support ligands to maintain cluster stability. An asymmetric ligand environment may be the cause of cluster rearrangement, and in this regard,

TABLE 2

Neopentane Reaction Selectivity on Conventional and Cluster-Derived Catalysts
(Reactant Gas: 1.3 kPa Hydrocarbon, 13 kPa H_2 , balance helium to 101 kPa; total conversion $\leq 10\%$)

Catalyst	Wt%	H/Pt(T)	Activation treatment	T(K)	$R_{\text{isom}}/R_{\text{hydr}}$
Pt ₁₅ /DA	1.59 Pt	0.40	H ₂ , 623 K, 3 hrs	623	0.2
Pt ₁₅ /DA	1.59 Pt	(0.30) ^b	H ₂ , 1023 K, 3 hrs	623	1.2
Pt/alumina ^a	5.51 Pt	0.57	H ₂ , 770 K, 3 hrs	573	0.5
Pt/alumina ^a	7.62 Pt	0.17	H ₂ , 770 K, 3 hrs	573	2.2

^a Prepared via incipient wetness impregnation using hexachloroplatinic acid and stannous chloride solutions.

^b Dispersion estimate from TEM.

the cluster may be seen as more of a flexible framework than a well-defined crystallite. A high-resolution electron microscopy study of $\text{Rh}_6(\text{CO})_{16}$ deposited onto a spinel-type alumina was conducted by Iijima and Ichikawa (24). The sample had been treated *in vacuo* at 423 K, which presumably had completely decarbonylated the clusters. Isolated metal deposits imaged on top of (111) support faces existed in two different sizes, both hemispherical in shape. One size was comparable to a 6-atom cluster, and the other was slightly larger, possibly resulting from condensation of two or three 6-atom clusters. The alumina support reportedly contained few surface hydroxyls, and the stabilization must have occurred by interaction of rhodium atoms with Lewis acid-base sites. When the electron microscopy results are taken in conjunction with the evidence for reversible recarbonylation of $\text{Rh}_6(\text{CO})_{16}$ on alumina (25), it seems that the metal framework will reconform to a changing ligand environment, provided that the metal-support bonds are strong enough to restrict metal mobility and prevent metal agglomeration but not to irreversibly oxidize metal atoms.

During impregnation of the $\gamma\text{-Al}_2\text{O}_3$ thin film by $\text{Pt}_{15}(\text{CO})_{30}^{2-}$, metal carbonyl cluster stability could be achieved by an abundance of surface hydroxyl groups. The high magnification micrographs (Fig. 5) indicate that small clusters of platinum with sizes near 1

nm (e.g., 15-atom units) have been stabilized where the clusters have been deposited with adequate spacing. The 1-nm sized Pt features seen in TEM micrographs could be used as evidence for 15-atom intact clusters. Due to resolution limitations, a distinction could not be made on whether such features were rod like (corresponding to the Pt_{15} metal carbonyl cluster framework) or spherical, as expected for a minimum energy configuration. It is probable that the air exposure during handling removed the CO ligands. In the air-contaminated $\text{Pt}_{15}/\text{PDA}^*$ and $\text{Pt}_{15}/\text{DA}^*$ slurry samples, only a weak carbonyl band was observed following preparation. In contrast, the glove-box prepared sample Pt_{15}/DA showed strong CO bands. Therefore, the metal cluster probably rearranged upon exposure to air. A hemispherically shaped cluster containing 15 Pt atoms would have a diameter of about 1 nm, and this size would be consistent with the TEM results for the freshly wetted sample.

In the infrared spectroscopy experiments involving samples prepared by *in situ* impregnation, the cluster dianion seemed to be stable in a weakly adsorbed state for at least several hours. For the slurried samples, the cluster rearrangement to bulk-like form took place after three days of contact, as evidenced by the color change from green to brown. The specimens prepared by *in situ* impregnation show that upon heating, the weakly adsorbed species are also trans-

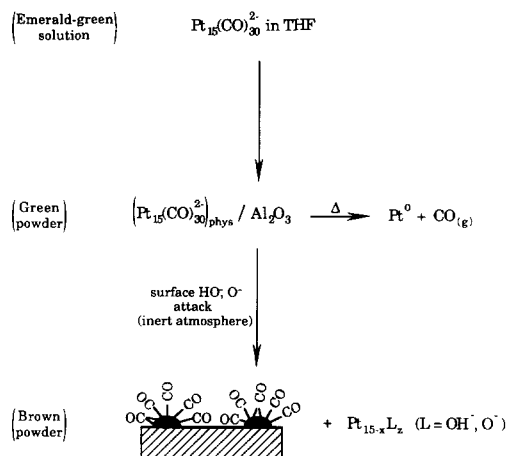


FIG. 6. Schematic representation of thermal decomposition of $\text{Pt}_{15}(\text{CO})_{30}^{2-}$ on aluminum oxide.

formed toward a bulk-like form as decarbonylation commenced with the disappearance of the μ_2 -CO band at 340 K. Attempts to reverse the decarbonylation at this stage by exposure to 100 kPa CO and cooling to room temperature were unsuccessful, since the infrared spectrum of $\text{Pt}_{15}(\text{CO})_{30}^{2-}$ could not be regenerated. The transformation of the cluster appears to be related to the presence of surface hydroxyl groups, since the cluster compound was stable to a higher temperature (near 370 K) on the dehydroxylated alumina support. Particle agglomeration did not occur in air-stored samples, which slowly became olive-green after several weeks of storage. The green color probably coincides with formation of a hydrated platinum surface complex. The course of the decomposition process of $\text{Pt}_{15}(\text{CO})_{30}^{2-}$ on alumina is diagrammed in Fig. 6.

The platinum clusters in the air-contaminated, slurried samples maintained considerable CO chemisorption capacity, as shown by the strong t-CO bands that appeared with initial exposure to CO gas before thermal treatment. Following thermal treatments, regenerated CO bands are not as intense as in the initial exposure. This may be due to slight particle agglomeration and interaction with surface contaminants

introduced by cracked solvent molecules on the alumina surface. Considerable adsorption capacity was restored by mild reduction treatment. Desorption of CO with increasing temperatures is consistent with the behavior of highly dispersed platinum, i.e., the t-CO peak is seen to weaken and shift to lower frequency. Additional bands are observed in the spectra of the slurried catalysts following desorption at temperatures above 473 K. These bands are weak (2088 cm^{-1} and 2165 cm^{-1}), and it is possible that they may also be present in spectra containing the intense t-CO Pt band. The peaks are assigned to metal carbonyl bands in which the platinum is in a positive oxidation state. Upward shifts in the t-CO stretching band are expected when the metal center becomes electron deficient. Such an electron withdrawal could come either from oxidative addition to the metal via hydroxyl attack, or from a Lewis acid site that withdraws charge from the metal electron cloud. In either case, the charge withdrawal will diminish back bonding from metal to CO ligands, resulting in a stronger C-O bond, but weaker Pt-CO bond. The appearance of these bands may be due to residual CO gas trapped in stagnation areas of the treatment cell, which readsorbed on the sample upon cooling.

Neopentane conversion over Pt_{15} cluster-derived catalyst showed high hydrogenolysis selectivity following reduction at 623 K. This is consistent with enhanced cracking relative to isomerization characteristic of highly dispersed platinum. Ichikawa (11) observed that the ratio of isomerization to hydrogenolysis activity (S_1) was equal to 0.25 over catalysts derived from $\text{Pt}_{15}(\text{CO})_{30}^{2-}$, in contrast to selectivity ratios ranging from 0.01 to 0.1 over catalysts derived from the smaller Pt_3 dianion subunits. The selectivity obtained in the present study for Pt_{15}/DA at 623 K ($S_1 = 0.2$) is in agreement with the result of Ichikawa, suggesting some structure retention to this temperature. The isomerization activity increased

to $S_1 = 1.2$ following catalyst treatment at 1020 K for 3 h. This selectivity is normally associated with large crystallites, as seen by comparison with the results on conventionally prepared Pt samples; however, sintering was not detected by STEM analysis. Thus, it is probable that low temperature catalyst treatment, starting from the 15-atom clusters, could create small Pt particles with an abundance of low-coordination surface Pt atoms. A high-temperature treatment would recrystallize the particle, forming smoother planar facets. Indeed, the results of this study show that the amount of bridge-bonded CO on cluster-derived catalysts is larger than for conventionally prepared Pt catalysts, suggesting that these derived catalysts retain some special surface properties.

In summary, Pt_{15} clusters are retained on the surface of alumina after impregnation under inert atmosphere. These clusters are decarbonylated irreversibly upon exposure to air at room temperature. Irreversible rearrangement of the initial cluster framework takes place upon heating to near 340 K on hydroxylated alumina, whereas this process takes place near 370 K on dehydroxylated alumina. This rearrangement commences with the removal of the bridge-bonded μ_2 -CO ligands, followed by progressive weakening and red-shifting of the terminally bonded t-CO ligands. Reexposure to CO gas failed to regenerate the precursor compound. The Pt clusters formed at these temperatures maintain a tendency to form a higher amount of bridge-bonded CO compared to conventionally prepared Pt catalysts. The characteristic behavior of CO adsorbed on bulk-like Pt particles is finally achieved upon continued heating of the cluster-derived catalysts to near 500 K, at which point the Pt particle size has increased to 1.5–2.0 nm. Further heating to temperatures near 800 K leads to modest particle growth to sizes between 2.0 and 3.0 nm on high surface alumina. This high-temperature treat-

ment also leads to changes in Pt surface properties, manifested by an increase in the selectivity for neopentane isomerization compared to hydrogenolysis.

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