Platinum and Palladium on Silica Produced by Impregnation from Tetrakis(Triphenylphosphine) Complexes

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Platinum and palladium supported on silica have been obtained by the heat treatment of Pt [P(C$_6$H$_5$)$_3$]$_4$ and Pd [P(C$_6$H$_5$)$_3$]$_4$. The metal dispersion has been determined as a function of thermal treatment. Up to 400°C the degrees of dispersion of Pt and Pd are similar; at higher temperatures the sizes of Pt crystallites are greater than those of Pd.

INTRODUCTION

Platinum supported on silica is used as a retarding agent in the combustion of organosiloxane polymers, but palladium exhibits no effect. In order to verify whether this difference in behavior results from a difference of dispersion of platinum and palladium, dispersions of both metals on aerosils (silica obtained in gas phase by Degussa) have been prepared from tetrakis(triphenylphosphine)platinum and tetrakis(triphenylphosphine)palladium.

EXPERIMENTAL

Preparation of Complexes

Tetrakis(triphenylphosphine)platinum (0). The complex was prepared according to the procedure described by Ugo *et al.* (*1*): 15.4 g triphenylphosphine was dissolved in 200 ml of absolute methanol at 65°C. When the solution was clear, a solution of 1.4 g of potassium hydroxide in a mixture of 32 ml of ethanol and 8 ml of water was

added. Then 5.24 g of potassium tetrachloroplatinate(II) dissolved in 50 ml of water (0.0126 mole) was slowly added to the alkaline triphenylphosphine solution while stirring at 65°C. A pale yellow compound separated. After cooling, the compound was recovered by filtration, washed with 150 ml of warm ethanol, then with 60 ml of cold water, and again with 50 ml of cold ethanol. The resulting pale yellow powder was dried in vacuum for 2 hr and stored under pure nitrogen.

Tetrakis(triphenylphosphine)palladium (0). A mixture of 10.48 g of triphenylphosphine, 3.02 g of the acetylacetonate of palladium, and 600 ml ethanol was introduced into a Pyrex vessel under argon bubbling (*2*). The mixture was refluxed for an hour and then cooled down. The precipitate obtained was filtered under argon, washed with pentane, and dried under vacuum.

Characterization of Silica

Two silicas were used.

Acrosil 300 (silica A), obtained in the vapor phase, has a specific surface area of 300 m^2/g and shows no significant porosity.

270

TABLE 1

Characteristics of Silica Supports

	S_{BET} (m²/g)	d_A (Å)	OH (per 100 Å²)
Silica A	307	80	3.1
Silica B	260	80	0.9

^{a} S_{BET} is the specific surface area as determined by N_2 adsorption; d_A is the mean arithmetic diameter of particles as determined by electron microscopy; OH is the surface hydroxyl content as determined by the reaction with $TiCl_4$ (4).

ir bands resulting from OH groups are located between 3750 and 3300 cm^{-1}. An absorption band at 3750 cm^{-1} corresponds to "free" hydroxyl and a 3300 to 3700 cm^{-1} band to adsorbed water, internal and bonded hydroxyls (3).

Silica B was obtained by heat treatment of silica A with octamethylcyclotetrasiloxane (D_4) at 300°C for 0.5 hr. "Free" hydroxyl groups (ir 3750 cm^{-1}) are no longer present.

The 3300 to 3700 cm^{-1} ir band is less intense than that obtained with silica A.

Table 1 gives some characteristics of silicas A and B.

Impregnation of Complexes onto the Supports

Three grams of silica was mixed with the required quantity of platinum or palladium complexes dissolved in 40 ml benzene. The mixture was stirred overnight and the benzene was removed in a rotating evaporator. The obtained solid (precursor of the catalyst) was dried at 120°C for 16 hr.

Conversion of Precursors into Catalysts by Heat Treatment

The precursor was heated at 250°C for 16 hr. In the case of palladium, the catalyst still contained some traces of complexes as shown by elemental analysis (Table 2).

After a subsequent heat treatment at 400°C for an hour, the decomposition of

complexes into metals was achieved (Table 2).

Characterization of the Catalyst

Three methods have been used for the measurement or the comparison of the sizes of the metallic particles supported by silica.

Chemisorption of carbon monoxide. Adsorption was carried out at 30°C for pressures of CO lower than 7 Torr; the chemisorbed volume was obtained by extrapolation of the linear part of the isotherm to zero pressure. We verified that no carbon monoxide was chemisorbed on the supports.

For the systems considered, stoichiometric ratios of metal/CO are not known with sufficient accuracy; chemisorption of CO has, therefore, been used to give relative values only.

Electron microscopy. Samples dispersed in methanol by utrasonics were deposited on grids. They were observed in phase contrast with a JEOL 100 B electron microscope. The final magnification of 2,000,000 was known to within 5%. The sample diameter was characterized by the mean arithmetic diameter of 1000 particles measured with a Zeiss TGZ3 semi-automatic size analyzer. This method, although valid for small metallic contents, becomes tedious for contents lower than 1% (a great number of micrographs is required for counting 1000 particles).

TABLE 2

Carbon/Metal Ratio as a Function of Heat Treatment

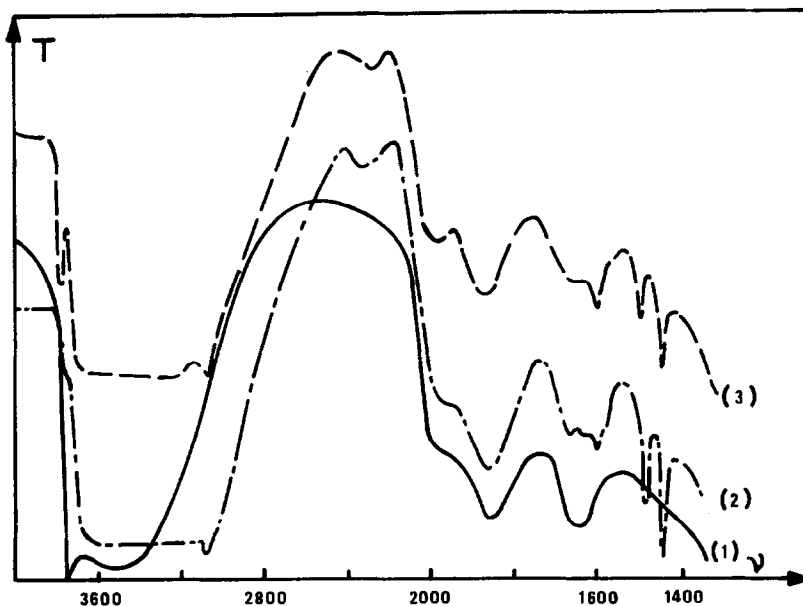| Temperature (°C)	Duration of heating (hr)	C/Pt	C/Pd
20	1	4.4	8.15
120	16	4.35	6.3
250	16	0	0.4
400	1	0	0

FIG. 1. Interaction between silica A and Pt $[P(C_6H_5)_3]_4$ or Pd $[P(C_6H_5)_3]_4$ complexes (heat treatment at 120°C for 16 hr). ir spectra: transmittance T (arbitrary units) as a function of wave-number ν (cm^{-1}). (1) silica A; (2) silica A + Pt $[P(C_6H_5)_3]_4$; (3) silica A + Pd $[P(C_6H_5)_3]_4$.

X-ray diffraction. A mixture of 10 parts catalyst and 1 part magnesium oxide was observed by X-ray diffraction. The (200) reflection of magnesium oxide and the (111) of platinum or palladium were registered. The average dimensions were determined by the Scherrer method (5). This technique is valid for samples containing more than 1% metal and for particles larger than 50 Å.

RESULTS AND DISCUSSION

Impregnation of Complexes onto Supports

A few minutes after mixing with silica A, the zero valence complex of platinum turns from golden yellow to white. In the case of palladium, immediately after mixing, the color goes from light yellow to deep red. It appears that an interaction of a chemical nature occurs between metallic complexes and silica A, as pointed out for $[Me(NH_3)_n]^{2+}$ by Dorling *et al.* (6) and Samanos (7).

We have studied this interaction by infrared spectroscopy using a Beckman

IR 20 spectrometer. Impregnated silicas compressed under 98 MPa were used for wave-numbers higher than 1300 cm^{-1}. For wave-numbers between 250 and 1300 cm^{-1}, they were mixed with 99% in weight of cesium bromide.

In the case of silica A, Fig. 1 permits the following observations:

(1) The intensity of the free hydroxyl band of silica decreases after treatment with metallic complexes. The decrease is more important with the platinum than with the palladium complex.

(2) The OH band shifts towards the frequency of bonded OH.

(3) A wide band appears with a maximum around 2260 cm^{-1}.

(4) Bands characteristic of the metal-phosphorus (ca. 420 cm^{-1}) and phosphorus-benzene bonds (3060, 1590, 1480, 720, and 690 cm^{-1}) are observed.

Malatesta *et al.* (*2, 8, 9*) and Fischer and Werner (*10*) pointed out that the zero valent complexes of platinum and palladium in benzene solution dissociate according to
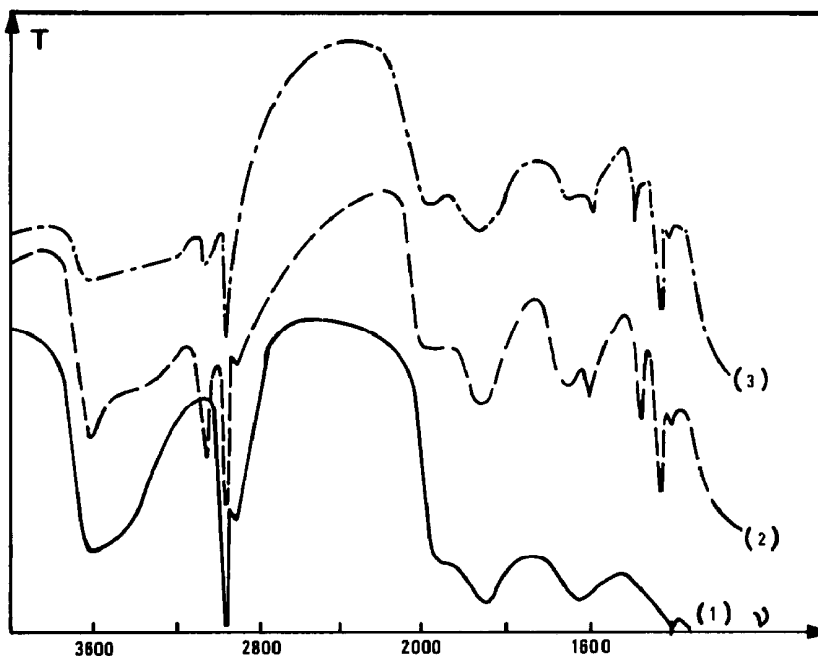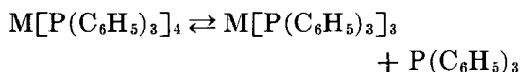
FIG. 2. Interaction between silica B and Pt $[P(C_6H_5)_3]_4$ or Pd $[P(C_6H_5)_3]_4$ complexes (heat treatment at 120°C for 16 hr). ir spectra: transmittance T (arbitrary units) as a function of wavenumber ν (cm^{-1}). (1) silica B; (2) silica B + Pt $[P(C_6H_5)_3]_4$; (3) silica B + Pd $[P(C_6H_5)_3]_4$.

the reaction:

$$M[P(C_6H_5)_3]_4 \rightleftarrows M[P(C_6H_5)_3]_3 + P(C_6H_5)_3$$

where M = Pt or Pd.

Cariati et al. (11) and Roundhill et al. (12) showed that zero valent complexes of platinum and palladium with an excess of negative charge on the metal behave as a base with weak or strong acids. For platinum they proposed the following sequence:

$$[PtL_4] \overset{-L}{\rightleftarrows} [PtL_3] \overset{HA}{\rightleftarrows} [PtHL_3]A$$
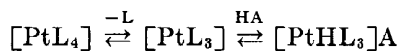
where L = Ligand and HA = weak or strong acid.

The vibration of the Pt–H valence for platinum hydride is observed for wave numbers between 2080 and 2280 cm^{-1} depending on the acid involved.

The decrease of intensity of the free OH band, the increase of the bonded OH band, and the appearance of a band at 2260 cm^{-1} are in agreement with the formation of a

complex of the following type (13)
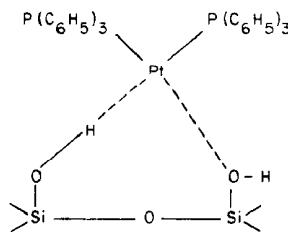
For silica B, results are reported in Fig. 2. Silica B does not contain free OH but only internal and bonded OH. It appears that the better resolution of internal OH results from the tendency of bonded OH to react with complexes of platinum and palladium. This is in agreement with the color change observed when these complexes are added to silica B. The absence of free OH, however, is a limitation to the interaction between the complexes and silica B.

According to ir spectroscopy the interaction between metal and silica is higher for platinum than for palladium. This result

TABLE 3

Volume of Chemisorbed Carbon Monoxide as a Function of Percentage by Weight of Metal of the Catalyst (Silica A)

Metal	Metal weight percentage[a]	CO chemisorbed (cm³/g metal)
Pt	0.24	40
	1.02	45
	2.21	43
Pd	0.23	74
	1.07	78
	2.12	71

[a] Determined by X-ray fluorescence.

disagrees somewhat with the usual reactivity of these complexes: According to Peloso (14), Pd[P(C₆H₅)₃]₄ is more reactive than Pt[P(C₆H₅)₃]₄.

Average Diameters of Metal Particles

The amount of chemisorbed carbon monoxide has been determined for platinum and palladium catalysts obtained by heating at 250°C for 16 hr (Table 3).

Metal dispersion is not affected by metal content in the domain considered. Therefore, the particle sizes can be determined using techniques appropriate for a sample with a metallic content of 1% or more, namely, electron microscopy and X-ray diffraction.

Results obtained by electron microscopy appear in Table 4. The dispersion is equivalent to that obtained by Dorling *et al.*

TABLE 4

Arithmetic Mean Diameter d_A of Metallic Particles on Silica

Metal	Metal weight percentage	d_A (Å) Silica A	d_A (Å) Silica B
Pt	1.02	12	12
Pd	1.07	18	18

TABLE 5

Particle Diameter as a Function of Temperature

Metal content	Temperature (°C)	Average diameters of crystallites (Å) Silica A	Average diameters of crystallites (Å) Silica B
Pt 1.02%	250	12[a]	12[a]
	400	28[a]	25[a]
	650	163[b]	160[b]
	800	310[b]	308[b]
Pd 1.07%	250	18[a]	18[a]
	400	29[a]	29[a]
	650	70[b]	75[a]
	800	138[b]	140[b]

[a] Value obtained by electron microscopy.
[b] Value obtained by X-ray diffraction

(6) and Samanos (7) using [Pt(NH₃)₄]²⁺ and [Pd(NH₃)₄]²⁺ as precursors for platinum and palladium. These authors attribute the good dispersion of metal to a chemical adsorption of metallic derivatives on active sites of silica, which is also the case for the precursors used in the present study, as previously pointed out.

Variation of Average Diameters of Metal Particles during Heat Treatment of Catalyst

After a preheating treatment at 250°C for 16 hr, the samples were heated at 400, 650, and 800°C for 1 hr. Table 5 shows the results obtained.

The dispersions of platinum and palladium are very similar until 400°C. At higher temperature the size of platinum crystallites is much greater than that of palladium.

CONCLUSION

For samples prepared at 400°C and below, the degrees of dispersion of Pt and Pd are close to each other. At 650°C and above, sintering is more important for platinum than for palladium. The sizes of Pt and Pd crystallites are, therefore, not

responsible for the difference between Pt and Pd in the flame retardance of organosiloxane polymers (14).

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