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Hydrogen Chemisorption and Surface Composition of Silica-Supported Platinum–Copper Alloys

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Silica-supported platinum–copper alloys were prepared as single-phase solid solutions. The surface composition of the alloy crystallites depends upon crystallite size: the larger the crystallite, the more the surface is enriched with copper. The surface composition of small crystallites (diameter <30 Å) approaches that of the interior of the crystallite.

INTRODUCTION

Recently, Sachtler and others have shown that the surface composition of metallic alloy films may not be the same as expected from random solid solutions and may differ from the composition of the interior of the film (*1*). The present work illustrates that similar effects can be observed in supported alloy crystallites as well. This observation casts some doubt on the validity of experimental studies of the catalytic activity of supported metal alloys.

EXPERIMENTAL METHODS

Catalyst Preparation

Two sets of alloys spanning the platinum–copper system were prepared, one with 5% by weight metal, the other with 0.55% by weight metal.

The 5% catalysts were prepared as follows: Davison grade 62 silica gel (see Table 1) was impregnated with a mixture of chloroplatinic acid and copper nitrate solutions having the metal composition of the alloy desired. The metal concentration of the impregnating solution was adjusted to give a total metal loading of 5% of the dry support in a volume of water slightly greater than the pore volume of the silica gel. (This relatively high metal loading was chosen to facilitate the X-ray analysis.) The impregnated gels were evacuated at 120°C for about 18 hr. They were reduced in flowing hydrogen at 480°C for 1 hr at atmospheric pressure immediately prior to use.

The 0.55% catalysts were prepared in the same way on Davison grade 950 silica gel. A gel of smaller pore size (see Table 1) and a lower metal loading were chosen to give well dispersed, small (<30 Å) metal crystallites (*2*).

X-ray Diffraction

Catalysts were examined by X-ray diffraction using a Norelco diffractometer and

TABLE 1
PHYSICAL PROPERTIES OF SILICA GELS[a]

Gel type	Surface area (m^2/g)	Pore vol. (cm^3/g)	Pore radius[b] (Å)
62	340	1.15	100
950	700	0.40	17

[a] Obtained from W. R. Grace and Co.

[b] Calculated from surface area and pore volume assuming spherical pores.

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copper $K\alpha$ radiation. (None of the 0.55% catalysts exhibited a diffraction pattern, suggesting that these catalysts had extremely small crystallite size.) Most of the 5% catalysts were found to be face-centered-cubic solid solutions with no detectable second phase. Those which exhibited a two-phase diffraction pattern were discarded.

The average metal crystallite size was determined for the 5% catalysts from the fine-particle-size broadening of the (111) diffraction peak using the Scherrer equation (*3*). Instrumental line broadening was determined in the angular range of interest from the width of the diffraction peaks of α-alumina with large crystallite size.

The metal surface area per gram of catalyst was calculated from the crystallite size assuming that the density of the alloy varies linearly with composition, that all of the crystallites are spherical, and that their entire surface is available for adsorption.

Electron Microscopy

Representative samples were examined with the electron microscope. (This work was performed by H. P. Studer of Shell Development Company, Exploration and Production Research Laboratory.) In order to verify the metal crystallite size determined from the X-ray diffraction patterns for the 5% catalysts, the particle size distribution was determined by direct measurement of the diameter of crystallites on the electron micrographs. Figure 1 shows that the X-ray crystallite size is in good agreement with the maximum in the particle size distribution curves determined from the micrographs.

Hydrogen Chemisorption

Hydrogen chemisorption was determined at 0°C in a mixed-gas (1% H_2 in argon) flow apparatus using the techniques described by Benesi and co-workers (*2*). Blank runs on each of the gels showed that there was no chemisorption of hydrogen on the 62 gel, but on the 950 gel there was an apparent negative chemisorption of 0.8 μmoles H_2/g. This is probably the result of physical adsorption of argon at 0°C. The hydrogen chemisorption measurements were corrected for the support contribution.

RESULTS AND DISCUSSION

Experimental Variation of Metal Crystallite Size

During the preparation of the 5% Pt–Cu catalysts for this study, it became ap-

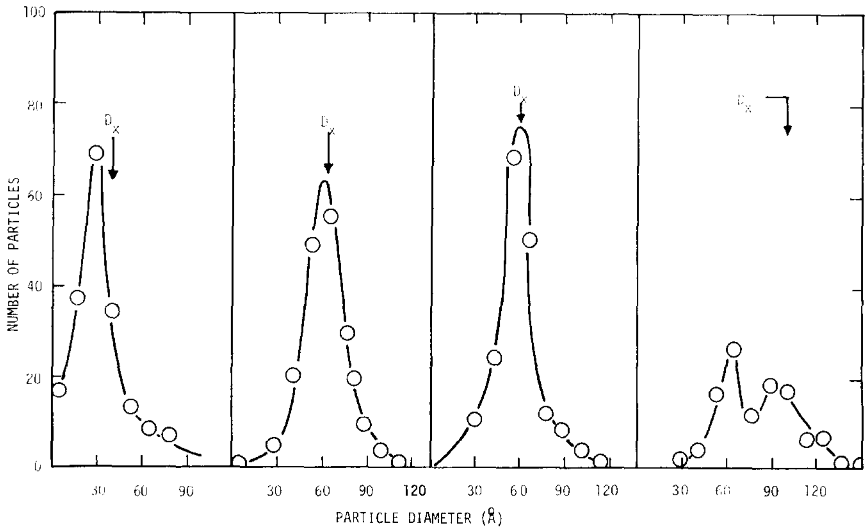

FIG. 1. Particle size distributions for 14% Cu, 86% Pt catalysts by electron microscopy; X-ray diameter $= D_x$.

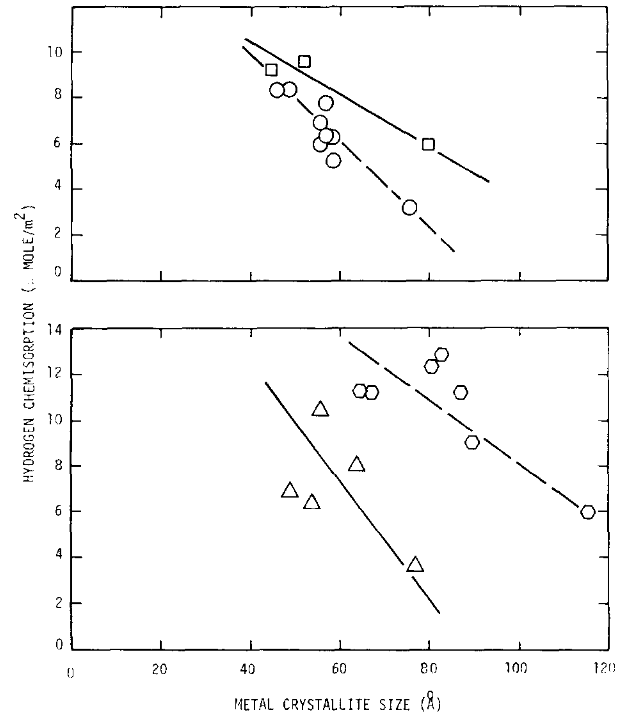

FIG. 2. Hydrogen chemisorption by platinum–copper alloys as a function of crystallite size: □, 14% Cu–86% Pt; ○, 25% Cu–75% Pt; ◯, 9% Cu–91% Pt; and △, 19% Cu–81% Pt.

parent that the catalyst treatment prior to reduction was important in determining the size of the metal crystallites obtained. It was observed that the catalysts which had been exposed extensively to laboratory air between catalyst drying and reduction had larger crystallites than those which were reduced immediately after drying. It was also observed that catalysts which were reduced in 1–2-g batches had smaller crystallites than those reduced in 10–20-g batches. Both of these effects are probably the result of differences in water content of the catalyst at the time of reduction. In the first case, water was readsorbed on the catalyst during exposure to laboratory air prior to reduction. In the second case, the drying of the catalysts continued in the hydrogen flow system as the temperature was raised to the point where reduction occurred. Therefore, one would expect, at a constant H_2 flow rate, the small catalyst batch to be drier at the time of reduction than the larger batch. In both cases the "wettest" catalyst gave the largest crystallites.

The water hypothesis was verified by a control experiment in which a batch of catalyst was prepared and divided into two parts. One portion was exposed to laboratory air for 24 hr before reduction while the second was stored in a sealed container in a desiccator for 48 hr before reduction. The crystallite size of the "wet-reduced" sample was 116 Å; the crystallite size of the "dry-reduced" sample was 81 Å. Subsequently prepared catalysts stored in closed vials in a desiccator for several weeks and reduced in small lots did not exhibit large crystallite sizes. Thus, it appears that exclusion of water by drying serves to prevent crystallite growth. Other workers have reached similar conclusions (*4*). For the purpose of the present study, the effect of water was ideal. It provided a means for systematically varying the crystallite sizes of the alloy catalysts over a fairly wide range.

Crystallite Size Effects in Chemisorption

The specific hydrogen chemisorptions (μmoles of H_2 per m^2 of metal surface) of the alloy catalysts depend on the crystallite size (see Fig. 2). As the crystallite size increases the specific chemisorption decreases rapidly. Because of the reliability of the particle size measurements (±10%), illustrated by Fig. 1, and the hydrogen chemisorption measurements (±5–10%), the effect is definitely larger than experimental error. This decrease might be attributed to some effect of crystallite size (at constant surface composition) or to variation in alloy composition at the surface of the crystallites. The first explanation seems unlikely because we have found the specific chemisorption of pure platinum is independent of crystallite size. This would indicate that the effect is caused by a change in surface composition as the crystallite size is varied. Sachtler and Dorgelo (*1*) proposed recently that the surface of Cu–Ni alloy films is covered with a Cu-rich alloy of low catalytic activity. Similarly, the decrease in specific chemisorption, shown in Fig. 2, could be the result of increasing enrichment of the crystallite surface with Cu as the crystallite size increases.

A careful X-ray diffraction study of the supported Pt–Cu alloys strongly supports this suggestion. The diffraction patterns of the catalysts are consistent with the formation of Pt–Cu solid solutions. Throughout the range of compositions investigated no new diffraction lines appeared. Any of the known ordered structures (PtCu, Pt_3Cu, and Pt_7Cu) would be detectable if they were present since they have FCC structures with lattice parameters twice as large as the disordered structure (*6*).

The length of the unit cell edge (lattice

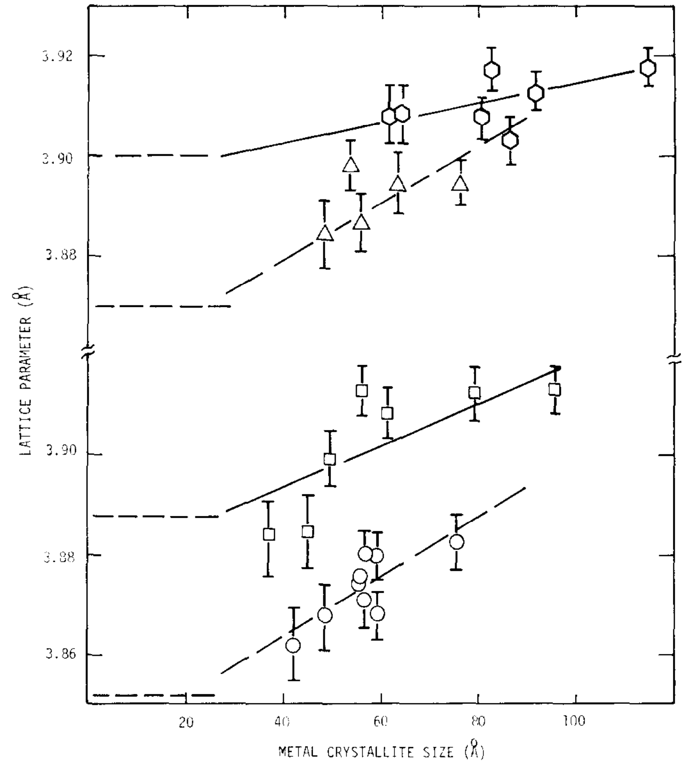

FIG. 3. Lattice parameters of platinum–copper alloys as a function of crystallite size: □, 14% Cu–86% Pt; ○, 25% Cu–75% Pt; ⬡, 9% Cu–91% Pt; △, 19% Cu–81% Pt; and - - -, Vegard's Law lattice parameter for each alloy composition (Pt lattice parameter = 3.91 Å, Cu = 3.615 Å).

parameter) of the alloy-crystallites was determined as a function of crystallite size. Several cases are shown in Fig. 3 where the experimental precision is indicated for each data point. The lattice parameters of the alloys increased with increasing crystallite size. This can be interpreted as follows: In binary solid solutions, the lattice parameter commonly varies linearly with composition (Vegard's Law). Since the lattice parameter of Pt is greater than that of Cu, an increase in lattice parameter of a Pt–Cu alloy implies a change in composition of the particles toward pure platinum. Thus, copper is apparently being excluded from the alloy crystallites as crystallite size increases. No new X-ray lines appear, indicating that the excluded copper or copper-rich regions must be well dispersed giving rise to no X-ray pattern of their own. This is consistent with the formation of a thin layer of copper (1 or 2 atoms thick) on the surface of the alloy. Such a layer would produce the observed decline in chemisorption and would be unobservable by X-ray diffraction.

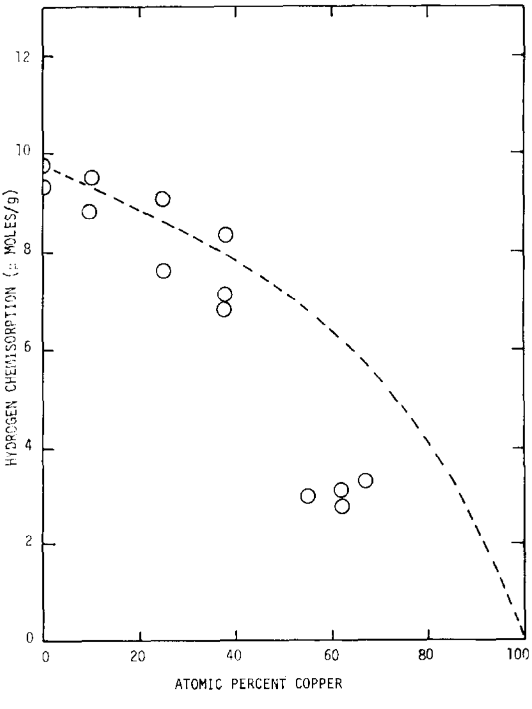

Fig. 4. Hydrogen chemisorption as a function of composition for copper–platinum alloys with small crystallites (<30 Å).

Sachtler and Jongepier (*7*) attributed Cu enrichment of the surface of the Cu–Ni films to a miscibility gap in the Cu–Ni system at low temperatures. Since the heat of mixing is negative for forming Pt–Cu alloys (*8*), the same argument cannot be used to explain the results reported here for supported Pt–Cu alloys. In the case of supported Ag–Rh alloys (where phase separation would be expected as in the Ni–Cu system), two crystalline phases were observed, Ag and Rh (*9*). The surfaces of the Rh crystallites are covered with Ag, similar to the Ni–Cu results of Sachtler.

The amount of copper excluded from the alloy crystallites can be calculated approximately from the lattice parameter change assuming Vegard's Law applies. For example, in the case of the 25% Cu–75% Pt alloy the amount of copper excluded is equivalent to about 30% of a monolayer of copper atoms on the alloy surface of 40-Å crystallites and about 2 monolayers on the surface of 80-Å crystallites. Thus, the amount of copper excluded is sufficient to produce the nearly complete loss of chemisorption in the catalyst with 75-Å particles. These effects mask the composition dependence of hydrogen chemisorption.

The results of the X-ray studies shown in Fig. 3 suggest that small crystallites (<30 Å) have the same bulk and surface compositions. A reasonable extrapolation of the lattice parameters of larger alloy crystallites shows that, near 30 Å, the lattice parameter approaches that expected from Vegard's Law. This is to be expected since almost all of the atoms in such small particles are on the surface. This in turn suggests that it is possible to determine the composition dependence of the hydrogen chemisorption of platinum–copper alloys using catalysts with small alloy crystallites.

Composition Dependence of Chemisorption

The 0.55% catalysts described above were used for the composition dependence studies. The metal crystallites in all of these alloys were too small to be observed by X-ray diffraction. Therefore, X-ray phase composition determinations could not be made. However, it was inferred by extrapolation from the behavior of the larger particle catalysts that the metal crystallites are single-phase solid solutions.

Hydrogen chemisorption by the 0.55% catalysts is shown in Fig. 4. The value of the chemisorption for pure platinum demonstrates that the platinum is well dispersed (crystallite size <30 Å). Experience with platinum and platinum–copper alloys with 5% metal loading and larger crystallite sizes has shown that for a given preparation procedure platinum–copper alloys have about the same crystallite size as pure platinum. The absence of an X-ray diffraction pattern in these catalysts confirms their small crystallite size. Therefore, it is assumed that, for the 0.55% catalysts, platinum–copper alloys have the same crystallite size as pure platinum. Thus, the effects described above are attributed to changes in alloy composition and not to surface area changes.

These data show that the copper does not simply dilute the platinum atoms without changing their properties. For if it did, copper–platinum alloys should have hydrogen chemisorption proportional to the platinum content of the catalyst as shown by the broken line in Fig. 4.

It is possible, however, that the composition dependence of the hydrogen chemisorption by platinum–copper alloys is related to their electronic structure in a way similar to that proposed by Lyubarskii *et al.* (*5*) for nickel–copper alloys. The platinum–copper system is electronically similar to the nickel–copper system. The *d*-band of platinum–copper is, like nickel–copper, completely filled at about 60 atomic percent copper and, as with nickel–copper, chemisorption becomes very small above this copper content. This suggests that platinum–copper alloys may require vacant *d*-electron levels in order to chemisorb hydrogen.

CONCLUSIONS

The dependence of surface composition on crystallite size observed in this work illustrates the need for careful characterization of catalysts. Some of the contradictory conclusions about the composition dependence of catalytic activities of alloys which have been reported are probably the result of differences in the surface composition of the catalysts studied. The present work illustrates that, in some cases, surface composition changes can be detected and avoided.

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