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Dispersion and Structure of Platinum–Iridium Catalysts

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A series of supported platinum–iridium catalysts was investigated by hydrogen chemisorption and X-ray diffraction. The catalysts all contained equal amounts of platinum and iridium by weight. Chemisorption measurements were made on both silica and alumina supported catalysts containing amounts of platinum plus iridium ranging from 0.6 to 20 wt%. For given contents of platinum and iridium, hydrogen chemisorption was higher on catalysts supported on alumina, indicating a higher degree of metal dispersion on alumina than on silica. X-ray diffraction measurements were limited to silica supported samples with platinum plus iridium contents ranging from 5 to 20 wt%. The presence of platinum–iridium bimetallic clusters is evident from the diffraction patterns, which exhibit diffraction lines at positions approximately midway between the positions of the corresponding lines for platinum and iridium metals. X-ray diffraction studies on alumina supported samples are complicated by interference from the diffraction pattern of the alumina.

INTRODUCTION

In recent years supported bimetallic systems have been investigated as catalysts (*1–3*). Examples of systems which have been studied in our laboratories are ruthenium–copper and osmium–copper supported on silica (*1*). In these catalysts the metallic component consists of small bimetallic clusters dispersed on the silica carrier. The ruthenium–copper and osmium–copper clusters are examples of a class of bimetallic clusters consisting of atoms of a Group VIII and a Group IB metal. Another type of bimetallic cluster of interest is composed of atoms of two metals from Group VIII, as exemplified by platinum–iridium (*2*). This type of cluster is an active component of catalysts employed in the reforming of petroleum naphthas (*2, 4*). The present paper is concerned with chemisorption studies of the dispersion of supported platinum–iridium clusters and with the characterization of some of these catalysts by X-ray diffraction.

EXPERIMENTAL

Apparatus and procedure. The apparatus for the gas adsorption measurements has been described elsewhere (*5*). Briefly, it consists of a conventional high-vacuum system capable of being evacuated to a pressure of 10^{-6} Torr. The amount of adsorption is determined volumetrically. After the catalysts are reduced in a stream of hydrogen at 500°C in the adsorption cell, the system is evacuated and cooled to room temperature prior to obtaining an adsorption isotherm.

X-ray diffraction measurements on the catalysts were made with a Philips vertical diffractometer employing CuKα radiation. The X-ray tube was operated at a voltage of 45 kV and a tube current of 35 mA. The diffractometer utilized a diffracted-beam,

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curved graphite crystal monochromator in conjunction with a pulse height analyzer to achieve wavelength selection. The detector was a scintillation counter with standard counting electronics. The diffractometer was controlled by a scan controller so that either analog (strip chart) or digital (step scan) data could be recorded. Both analog and digital information were used in the study.

Materials. The platinum–iridium catalysts used in this work were prepared by a simple impregnation procedure using mixed aqueous solutions of chloroplatinic and chloroiridic acids (*2*). The catalysts used in the X-ray diffraction studies were supported on a form of silica known as Cab-O-Sil HS5 (300 m^2/g surface area), obtained from the Cabot Corporation, Boston, Massachusetts. Approximately 2.2 ml of impregnating solution, with appropriate concentrations of chloroplatinic and chloroiridic acids, was employed per gram of silica. After impregnation, the resulting material was dried at 110°C and subsequently reduced in a stream of hydrogen at 500°C. Chemisorption data were obtained on samples reduced *in situ*, while the X-ray diffraction data were obtained on reduced samples subsequently exposed to the atmosphere. In the preparation of platinum–iridium catalysts with alumina as the support, a smaller amount of impregnating solution was used, about 0.65 ml per gram of alumina. The alumina was prepared by heating β-alumina trihydrate at 600°C for 4 hr and had a surface area of approximately 200 m^2/g. Catalysts consisting of platinum or iridium alone on a support were prepared in the same manner as the bimetallic catalysts, the only difference being that the impregnating solution contained the acid precursor of only one of the metals.

RESULTS

Hydrogen chemisorption data were obtained at room temperature on all of the platinum–iridium catalysts. After an adsorption isotherm such as that labeled *A* in Fig. 1 was completed, the adsorption cell was evacuated at room temperature for 10 min. This procedure removed the weakly chemisorbed hydrogen, the amount of which was then determined by running a second isotherm such as that labeled *B* in Fig. 1. The difference between the total chemisorption represented by isotherm *A* and the weak chemisorption represented by isotherm *B* is the strong chemisorption ($A - B$ in Fig. 1). It is useful to express the adsorption data in terms of the quantity H/M, which represents the number of hydrogen atoms adsorbed per atom of metal (platinum + iridium) in the catalyst. In the case of total chemisorption the value of H/M depends on the pressure, while for strong chemisorption it is virtually independent of pressure. Values of H/M are consistently higher for alumina supported platinum–iridium than for silica supported platinum–iridium, as shown in

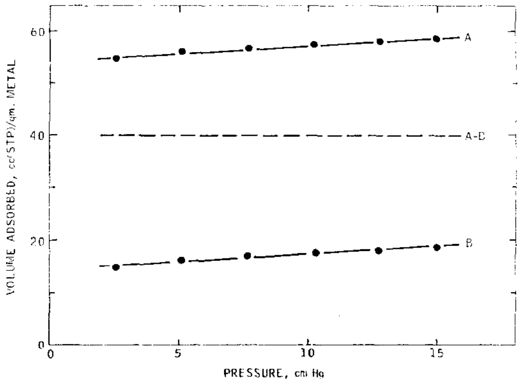

FIG. 1. Typical adsorption isotherms at room temperature for hydrogen on a silica supported platinum–iridium catalyst containing 1.25 wt% each of platinum and iridium. Isotherm *A* represents the total adsorption of hydrogen on the catalyst after reduction and evacuation at 500°C. Isotherm *B* represents the weakly adsorbed hydrogen, determined by running a second isotherm after evacuation of the sample for 10 min at room temperature following the completion of isotherm *A*. The difference between the isotherms, $A - B$, represents strongly adsorbed hydrogen.

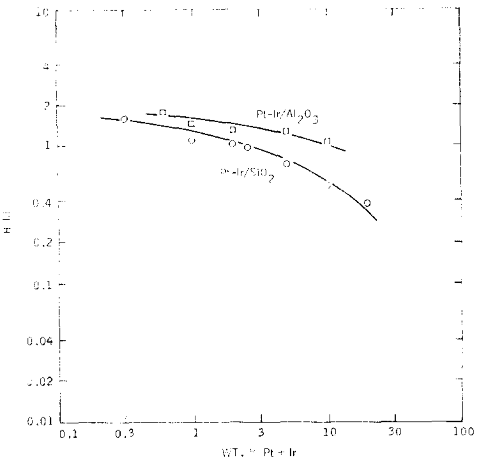

FIG. 2. Hydrogen chemisorption at room temperature on platinum–iridium catalysts as a function of the platinum plus iridium content. All the catalysts contain equal percentages by weight of platinum and iridium. The quantity H/M represents the ratio of the number of hydrogen atoms H adsorbed to the number of metal atoms M (platinum and iridium) in the catalyst and refers to the total chemisorption at an equilibrium pressure of 10 cm Hg. The upper curve is for alumina supported catalysts while the lower curve is for silica supported catalysts.

Figs. 2 and 3 for catalysts containing equal percentages by weight of platinum and iridium at a variety of metal loadings. For both total and strong chemisorption, the value of H/M increases with decreasing metal concentration in the catalyst. From the data in Fig. 2 it can be seen that H/M values for total chemisorption frequently exceed unity, especially in the case of the alumina supported catalysts (*6*). Values of H/M as high as 1.7 (at an equilibrium pressure of 10 cm Hg) are observed at the lowest metal concentrations for platinum–iridium supported on alumina. In the case of the strongly chemisorbed fraction, H/M appears to approach a limiting value near unity as the metal concentration is decreased below about 1 wt%. At these low metal concentrations we assume that all of the platinum and iridium atoms are surface atoms. Electron microscopy data on such catalysts show the average diameters of the metal clusters to be of the order of 10 Å or smaller. Clusters of this size necessarily consist almost exclusively of surface atoms. The stoichiometry of the strongly chemisorbed fraction therefore corresponds closely to one hydrogen atom per surface metal atom. Thus, the value of H/M for the strongly chemisorbed fraction is taken as a direct measure of the dispersion, which is defined as the ratio of surface atoms to total atoms in the metal clusters.

X-ray diffraction data were obtained on some of the platinum–iridium catalysts. Both platinum and iridium crystallize as fcc structures, and they form solid solutions in all proportions in the bulk (*7*). The lattice parameter is a function of the composition of the solid solution (*7*), as shown in Fig. 4. Thus, measurements of lattice parameters provide a way of demonstrating the presence of bimetallic clusters of platinum and iridium in the catalysts. However, it is extremely difficult or impossible to obtain satisfactory diffraction patterns on highly dispersed metal catalysts in which the metal dispersion approaches unity. The lines in the diffraction pattern are then extremely broad and weak, be-

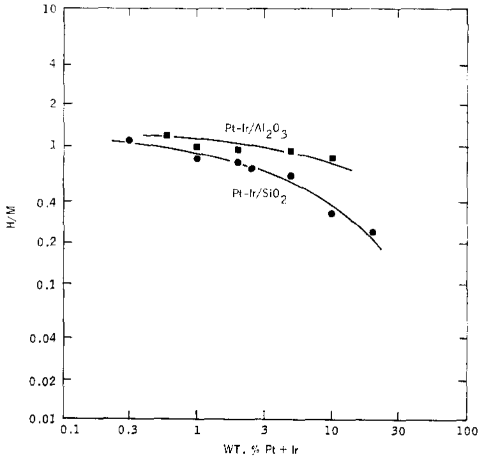

FIG. 3. The strongly chemisorbed fraction of the total hydrogen adsorption shown in Fig. 2. The quantity H/M defined in Fig. 2 now refers to the number of adsorbed hydrogen atoms retained per atom of metal (platinum and iridium) in the catalyst after evacuation at room temperature for 10 min.

coming indistinguishable from the background. In the present work, we have therefore not been able to employ X-ray diffraction to investigate platinum–iridium clusters in catalysts with metal dispersions approaching unity. However, we have found the method to be useful for investigating platinum–iridium clusters in catalysts with metal dispersions of about 0.60 and lower, when the clusters are supported on silica. The interpretation of the data is relatively straightforward for silica supported platinum–iridium clusters because the diffraction pattern of the silica does not interfere significantly with the diffraction pattern of the clusters. This statement is not true for the alumina supported clusters, and hence the data to be presented here are limited to clusters supported on silica.

The platinum–iridium catalysts investigated by X-ray diffraction had metal dispersions ranging from 0.24 to 0.75, as determined from hydrogen chemisorption data. The average sizes of the platinum–iridium clusters determined from the X-ray linewidths ranged from 49 to 27 Å. Data on metal dispersions, metal cluster sizes, and lattice parameters are summarized in Table 1. The intensities of the diffraction lines for the platinum–iridium clusters in these catalysts were, in general, lower than would be expected if the platinum and iridium in the catalysts were present exclusively as large metal crystallites with properties of the bulk metals. It appears that a fraction of the clusters is characterized by a dispersion close to 1 and does not contribute to the intensities of the observed diffraction lines. This fraction increases as the overall measured dispersion increases.

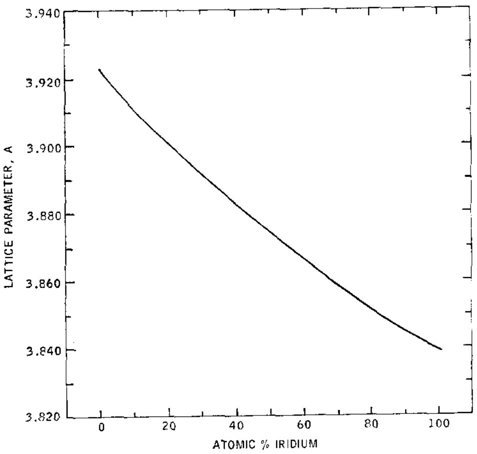

Fig. 4. Lattice parameter of platinum–iridium solid solutions as a function of composition [data from W. B. Pearson (7)].

TABLE 1

Properties of Platinum–Iridium Bimetallic Cluster Catalysts Investigated by X-Ray Diffraction

Concentration (wt%)[a]		Dispersion[b]	Cluster size[c] (Å)	Lattice parameter[d] (Å)
Pt	Ir			
10	10	0.24	49	3.875
5	5	0.32	35	3.875
2.5	2.5	0.60	27	3.890
1	1	0.75	—[e]	—[e]

[a] Platinum–iridium clusters supported on silica.

[b] Ratio of surface Pt + Ir atoms to total Pt + Ir atoms, as determined by hydrogen chemisorption.

[c] From X-ray linewidths.

[d] Average value determined from positions of a number of diffraction lines.

[e] Diffraction lines too weak for reliable determination of these quantities.

X-ray diffraction data on silica supported platinum–iridium bimetallic catalysts with equal percentages by weight of platinum and iridium ranging from 10% Pt, 10% Ir to 2.5% Pt, 2.5% Ir (corresponding to a Pt/Ir atomic ratio very close to 1) are shown in the middle fields of Figs. 5 to 7. In each case a portion of the diffraction pattern is shown which includes the (220) reflection. Also shown in the upper field of each figure is the corresponding part of the diffraction pattern of a physical mixture of bulk platinum and bulk iridium diluted with silica. In the lower field of each figure is shown the same region of the diffraction pattern for a physical mixture of equal weights of silica supported platinum and silica supported iridium, the mixture con-

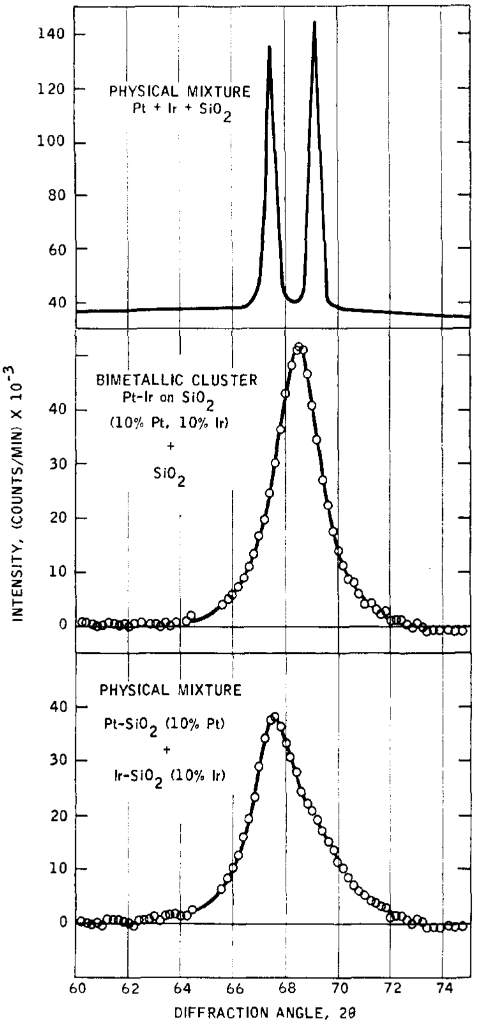

FIG. 5. X-ray diffraction study of a platinum–iridium bimetallic cluster catalyst. The upper field is a reference pattern for a physical mixture of platinum and iridium metals diluted with silica. The middle field is a pattern for a silica supported platinum–iridium bimetallic cluster catalyst containing 10 wt% Pt and 10 wt% Ir, mixed with an equal weight of silica. The lower field is a pattern for a physical mixture of silica supported Pt clusters and silica supported Ir clusters, the catalysts containing 10 wt% Pt and 10 wt% Ir, respectively. The mixture was formulated to match the platinum and iridium contents of the sample in the middle field of the figure.

taining the same absolute amounts of platinum and iridium as the platinum–iridium bimetallic catalyst sample. In Fig. 5 it should be noted that the platinum–iridium bimetallic catalyst was diluted with an equal weight of silica. The X-ray diffraction measurements were made under identical instrumental conditions. The data were collected digitally over a range of

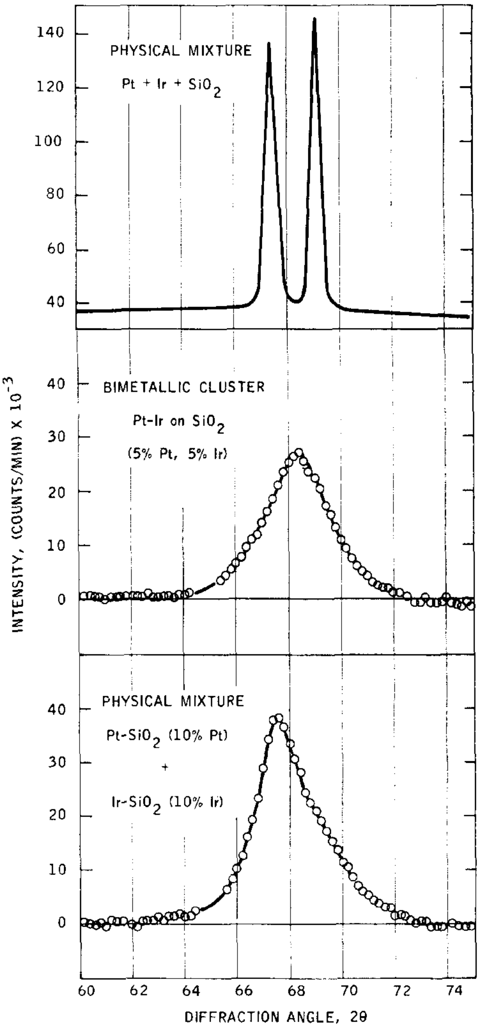

FIG. 6. X-ray diffraction study similar to that of Fig. 5, except that the platinum–iridium bimetallic cluster catalyst contained 5 wt% Pt and 5 wt% Ir and was not diluted with silica. The physical mixture of silica supported Pt clusters and silica supported Ir clusters employed in obtaining the pattern in the lower field of the figure contained the same absolute amounts of platinum and iridium as the platinum–iridium bimetallic cluster catalyst used in obtaining the pattern in the middle field.

diffraction angles (2θ) from 59 to 77° at increments of 0.2°. This relatively large size increment provided acceptable resolution because the line profiles were broad. In addition to the data shown in Figs. 5 to 7, data on the silica carrier itself were obtained over the same range of diffraction angles. The latter data showed that the silica contributed a sloping background in the region of the platinum–iridium diffraction lines. This background scattering arising from the silica carrier was subtracted from the total scattering in the diffraction patterns for the catalysts. In making the subtraction, it was necessary to scale the intensity of the silica alone to that of the catalyst in a range of diffraction angles (2θ) where the platinum–iridium clusters did not contribute to the measured intensities. For this purpose data points in the range of diffraction angles between 59 and 61° on one side of the diffraction line and between 75 and 77° on the other side of the diffraction line were employed. From these data points, a scaling factor was calculated and applied to each point in the diffraction pattern of the silica. A point-by-point subtraction of the scaled silica pattern from the catalyst pattern was then performed. This gave the diffraction pattern arising from the platinum–iridium clusters alone. A similar procedure was employed in obtaining the superimposed diffraction patterns of platinum clusters and iridium clusters in the physical mixtures of platinum–silica and iridium–silica catalysts.

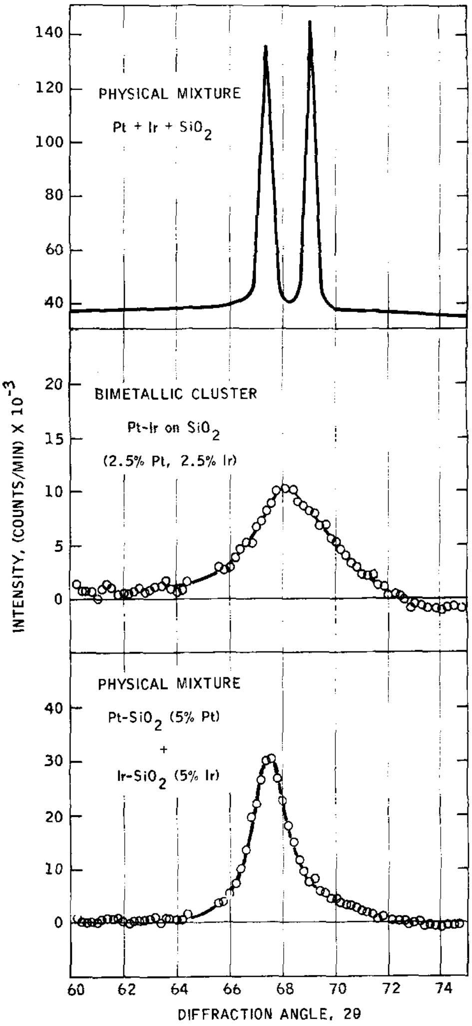

FIG. 7. X-ray diffraction study similar to that of Fig. 6, except that the platinum–iridium bimetallic cluster catalyst contained 2.5 wt% Pt and 2.5 wt% Ir. Also, the Pt–SiO$_2$ and Ir–SiO$_2$ components of the physical mixture contained 5 wt% Pt and 5 wt% Ir, respectively.

We now consider some of the features of the diffraction patterns in Figs. 5 to 7. In Fig. 5, for example, we see that the platinum–iridium bimetallic clusters in a catalyst containing 10% Pt and 10% Ir give a single (220) diffraction line (middle field of figure) about midway between the lines (upper field of figure) for bulk platinum and bulk iridium. The line for the clusters is broader than the lines for the bulk metals because of the small size of the clusters. Using the Scherrer equation [(*8*), p. 656] we calculate an average platinum–iridium cluster size of 49 Å from the line-width. The diffraction pattern of the physical mixture of silica supported platinum clusters and iridium clusters in the lower field of the figure consists of overlapping lines for the two individual types of clusters and is clearly different from that of the platinum–iridium bimetallic clusters. The overlap is due to the broadened nature

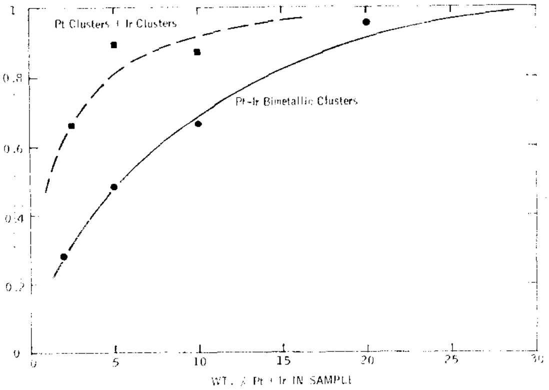

FIG. 8. Effect of the concentration of platinum plus iridium on the integrated intensity of the (220) diffraction line for silica supported platinum–iridium bimetallic cluster catalysts and physical mixtures of silica supported platinum clusters and iridium clusters. The intensity data are expressed as the ratio of the intensity I for the sample in question to the expected intensity I_M if the platinum and iridium in the sample were replaced by platinum and iridium metals.

of the individual lines resulting from the small sizes of the individual clusters of platinum and iridium, estimated to be 56 and 27 Å, respectively, from X-ray diffraction data on the individual catalysts. The foregoing discussion of the diffraction patterns in Fig. 5 also applies to the diffraction patterns in Fig. 6. The diffraction pattern of the platinum–iridium bimetallic clusters in Fig. 6 is for a catalyst containing half as much platinum and iridium (5% Pt, 5% Ir) as the corresponding bimetallic catalyst of Fig. 5. The linewidth is greater than that in Fig. 5, giving a lower average platinum–iridium cluster size of 35 Å. The lattice parameter of the platinum–iridium bimetallic clusters in the catalysts containing 10% Pt, 10% Ir and 5% Pt, 5% Ir is 3.875 Å, as determined from the positions of a number of different lines in the diffraction patterns (Table 1). This value corresponds to a composition of 50% Ir in Fig. 4, in agreement with the overall catalyst composition. When the platinum and iridium contents of the bimetallic cluster catalyst are decreased to 2.5% Pt, 2.5% Ir, the primary features of the diffraction patterns observed for the catalysts of Figs. 5 and 6 are retained, as shown in Fig. 7. However, the intensity of the (220) reflection corresponding to the diffraction line is substantially lower, and deviations of individual points about the line are more evident. From the linewidth, the average size of the platinum–iridium clusters is estimated to be 27 Å. Close inspection indicates that the position of the diffraction line has shifted somewhat, corresponding to an iridium content less than 50%. As shown by the data in Table 1, a lattice parameter of 3.890 Å is found for this catalyst, corresponding to a composition of 32% Ir in Fig. 4. Moreover, the intensity is only about half the intensity expected if the platinum and iridium in the catalyst existed only in the form of large metal crystallites. These results indicate the presence in the catalyst of iridium-rich bimetallic clusters which do not contribute to the intensity of the diffraction line and which are characterized by a higher metal dispersion than is representative of the catalyst overall.

It is of interest to consider data on the ratio of the intensity I of the (220) reflection for a platinum–iridium bimetallic cluster catalyst to the intensity I_M for a sample of the same composition in which the platinum and iridium are present as large metal crystallites with the properties

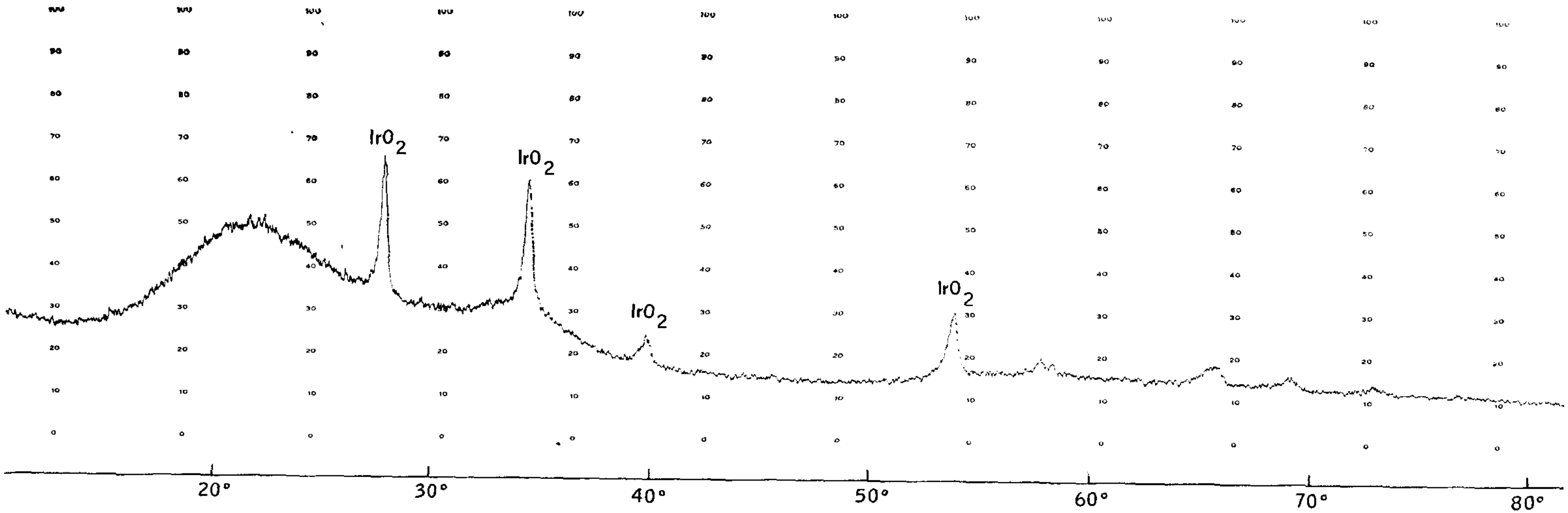

FIG. 9. X-ray diffraction scan on a silica supported platinum–iridium sample heated in air at 500°C. The sample contained 5 wt% Pt and 5 wt% Ir. Diffraction lines due to large crystallites (~290 Å) of IrO_2 *are observed.*

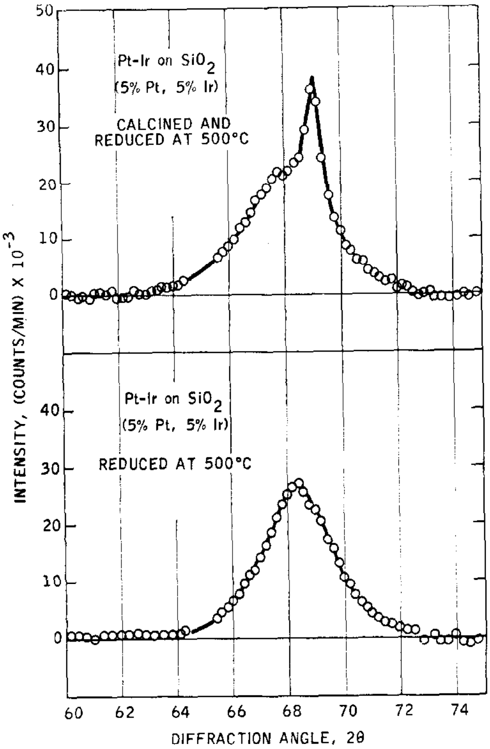

FIG. 10. X-ray diffraction pattern on the silica supported platinum–iridium sample of Fig. 9 after reduction in hydrogen at 500°C (upper field), indicating a mixture of large iridium crystallites and much smaller platinum clusters. A diffraction pattern on a silica supported platinum–iridium bimetallic cluster catalyst of the same composition is shown in the lower field for comparison.

of the bulk metals. The quantity I_M is determined from integrated intensities of the (220) reflection for pure platinum and iridium metals. With values of the mass absorption coefficients for the pure metals, the intensity of a 1/1 mixture of platinum and iridium was determined. This intensity, coupled with the mass absorption coefficient of silica, was then employed to determine I_M for a platinum–iridium–silica mixture with the same composition as a particular platinum–iridium bimetallic cluster catalyst or physical mixture of platinum–silica and iridium–silica catalysts. The method of determining intensities for mixtures is described by Klug and Alexander [(*8*), p. 544]. As shown by the data describing the lower curve in Fig. 8, the ratio I/I_M increases with increasing concentration of platinum and iridium in the catalyst. Also shown in Fig. 8 in the upper curve are similar data for physical mixtures of silica supported platinum clusters and iridium clusters, where I in this case refers to the total integrated intensity of the (220) reflections represented by the overlapping lines in the diffraction patterns. For the same amounts of platinum and iridium in a sample, the value of I/I_M is lower for the platinum–iridium bimetallic clusters than for the physical mixtures of separate clusters of platinum and iridium. These data indicate a higher metal dispersion in the case of the bimetallic clusters. Where chemisorption data are available for the components of the physical mixtures, they are consistent with this conclusion about metal dispersions derived from the X-ray data. For example, the platinum–iridium bimetallic cluster catalyst containing 2.5% Pt, 2.5% Ir has a metal dispersion of 0.60 compared to 0.40 for the physical mixture containing the same amounts of platinum and iridium.

In preparation of highly dispersed platinum–iridium bimetallic clusters in this investigation, the carrier (SiO_2 or Al_2O_3) is first coimpregnated with chloroplatinic and chloroiridic acids and then dried at a temperature of 110°C prior to reduction in hydrogen at 500°C. If the catalyst is heated in air (calcined) at too high a temperature, say 500°C, the iridium undergoes oxidation and agglomeration to form large crystallites of IrO_2. A diffraction scan on a silica supported Pt–Ir catalyst heated in air at 500°C exhibits lines due to IrO_2, as shown in Fig. 9. From the width of the line for the (110) reflection, at a diffraction angle (2θ) of 28°, the crystallite size is estimated to be about 290 Å. On subsequent reduction in hydrogen at 500°C, the IrO_2 crystallites are reduced to metallic iridium crystallites of similar size. At this point, the material consists of a mixture of a highly dispersed platinum or platinum-rich phase and large crystallites of iridium. The diffraction profile for the (220) region for this material is given in the upper field of Fig. 10. The contrast between this pattern and the pattern for platinum–iridium bimetallic clusters in the lower field of Fig. 10 is clear.

DISCUSSION

The presence of highly dispersed platinum–iridium bimetallic clusters in silica supported platinum–iridium catalysts is clearly evident from X-ray diffraction patterns. In the present work it has been possible to obtain such X-ray diffraction patterns for platinum–iridium clusters with average sizes in the range of 27 to 49 Å. The lower limit of this range corresponds to clusters in which about one-half of the total platinum and iridium atoms are present in the surface. It becomes very difficult to obtain satisfactory X-ray diffraction patterns for more highly dispersed platinum–iridium clusters. However, in related studies from this laboratory on alumina supported platinum–iridium catalysts, the presence of platinum–iridium bimetallic clusters in which essentially all of the platinum and iridium atoms are surface atoms is evident from Mössbauer spectroscopy data (*9*).

In the preparation and use of a platinum–iridium bimetallic cluster catalyst, exposure to oxygen at high temperatures may interfere with the production or maintenance of highly dispersed platinum–iridium clusters in the catalyst. In general, exposure to air at temperatures below about 375°C is not harmful, but contact with air at temperatures above about 450°C should be avoided (*2*). As the results in this paper show, exposure of a platinum–iridium catalyst to air at 500°C resulted in the formation of large IrO_2 crystallites which on subsequent reduction were converted to large crystallites of iridium. The catalyst then consists of a mixture of highly dispersed platinum or platinum-rich clusters and large crystallites of iridium.

The chemisorption results on the platinum–iridium catalysts indicate a higher dispersion of platinum–iridium clusters on alumina than on silica, for a given amount of platinum and iridium in a catalyst. Data were obtained showing the dependence of the quantity H/M, representing the number of hydrogen atoms chemisorbed per atom of metal (platinum + iridium), on the concentration of platinum and iridium in the catalyst. As the concentration of platinum and iridium decreases, the quantity H/M increases. In the case of total chemisorption at an equilibrium pressure of 10 cm Hg, values of H/M as high as 1.7 are observed at very low concentrations of platinum and iridium. This observation does not change much if one considers values of H/M obtained by extrapolation of adsorption isotherms to zero pressure, since the isotherms are only slightly pressure dependent over the range of pressures employed in obtaining the isotherms. Perhaps the adsorption stoichiometry changes when the dispersion of the platinum–iridium clusters becomes very high; i.e., some metal atoms in the surface (e.g., those at points of lower coordination number such as edge or corner atoms) may chemisorb more than one hydrogen atom. Since the fraction of such atoms present in the clusters increases with increasing dispersion, values of H/M substantially in excess of unity may be realized when essentially all of the metal atoms are surface atoms. From our experiments alone, we cannot discount completely the possibility of hydrogen "spillover" onto the support (*6*), but recent results of other workers in this laboratory on iridium catalysts suggest that the high H/M values are a consequence of adsorption stoichiometry rather than a spillover effect (*10*). In any case, for samples with very low concentrations of platinum and iridium, values of H/M corresponding to the amount of adsorbed hydrogen retained after the sample is evacuated at room temperature for 10 min ($\sim 10^{-6}$ Torr of pressure) subsequent to measurement of an isotherm are much closer to unity. Consequently, we have used H/M values determined in this way as a measure of the dispersion of the platinum–iridium clusters in the catalysts of this investigation.

REFERENCES

1. Sinfelt, J. H., *J. Catal.* **29**, 308 (1973).
2. Sinfelt, J. H., U.S. Patent 3,953,368 (1976).
3. Sinfelt, J. H., *Acc. Chem. Res.* **10**, 15 (1977).
4. Sinfelt, J. H., *Platinum Met. Rev.* **20** (4), 114 (1976).
5. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8**, 82 (1967).
6. Engels, S., Malsch, R., and Wilds, M., *Z. Chem.* **16**, 416 (1976).
7. Pearson, W. B., "A Handbook of Lattice Spacings and Structures of Metals and Alloys," p. 704. Pergamon Press, New York, 1964.
8. Klug, H. P., and Alexander, L. E., "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials," 2nd ed. Wiley, New York, 1974.
9. Sinfelt, J. H., U.S. Patent 3,953,368 (1976). The Mössbauer spectroscopy data in this patent were obtained with the collaboration of Dr. Robert L. Garten.
10. Kugler, E. L., McVicker, G. B., and Garten, R. L., Data to be published.