JOURNAL OF CATALYSIS 62, 127–139 (1980)

Structure of Pt–Ir Catalysts: Mössbauer Spectroscopy Studies Employing ^{57}Fe as a Probe

R. L. GARTEN[1] AND J. H. SINFELT

Corporate Research Laboratories, Exxon Research and Engineering Co., Linden, New Jersey 07036

Received May 17, 1979

The structure of an alumina-supported platinum–iridium catalyst containing 1.75 wt% each of platinum and iridium was investigated by incorporating into the catalyst a small amount (0.1 wt%) of ^{57}Fe as a probe for Mössbauer spectroscopy experiments. The Mössbauer data are consistent with the view that the catalyst contains highly dispersed bimetallic clusters of platinum and iridium, if the temperature of exposure of the catalyst to air during its preparation is not too high. Calcination in air at a temperature of 260C is very satisfactory in this respect, but a calcination temperature of 600C is too high. The use of the higher calcination temperature results in oxidation and agglomeration of the iridium, with the formation of large crystallites of IrO_2. Upon reduction, the catalyst may then be characterized approximately as a system containing two different types of metallic entities, one consisting of highly dispersed platinum or platinum-rich clusters and the other consisting of large iridium or iridium-rich crystallites. The results demonstrate the importance of preparative conditions in the formation of highly dispersed bimetallic clusters in the platinum–iridium system.

INTRODUCTION

Supported bimetallic clusters have been investigated as catalysts in recent years (*1*–*3*). One type of bimetallic cluster of interest is composed of atoms of two Group VIII metals, as exemplified by platinum–iridium (*2*). The presence of platinum–iridium bimetallic clusters with sizes in the approximate range of 25–50 Å has been demonstrated by X-ray diffraction studies on silica-supported platinum–iridium catalysts (*2*, *4*). However, when the platinum–iridium clusters are still smaller, it is difficult to obtain satisfactory diffraction patterns. The lines in the diffraction pattern are then very broad and weak and are not readily distinguished from the background. By contrast, Mössbauer spectroscopy studies may be conducted on platinum–iridium clusters in which virtually all of the metal atoms are surface atoms. In principle, such studies could be made by incorporating ^{195}Pt and/or ^{193}Ir Mössbauer isotopes in the catalysts. Experiments with these isotopes, however, are extremely difficult because of short lived sources and the requirement for measurements at liquid helium temperature. Alternatively, ^{57}Fe can be added to platinum–iridium catalysts as a sensitive Mössbauer probe of the interaction between platinum and iridium (*2*). The results of such an investigation on highly dispersed platinum–iridium clusters supported on alumina are reported in this paper. Catalysts of this type are of interest in the reforming of petroleum naphthas (*2*).

EXPERIMENTAL

Apparatus and procedure. The gas adsorption measurements were made in a conventional type of apparatus which has been described elsewhere (*5*). Briefly, the apparatus consists of a high vacuum system capable of being evacuated to a pressure of 10^{-6} Torr. The amount of gas adsorbed is determined volumetrically. After the catalysts are reduced in flowing hydrogen in the adsorption cell at 500°C, the system is

---

[1] Present Address: Catalytica Associates, Inc., 3255 Scott Blvd., 7-E, Santa Clara, California 95051.

0021-9517/80/030127-13$02.00/0

evacuated at 450°C and cooled to room temperature to obtain an adsorption isotherm.

The procedure employed in the Mössbauer experiments has been described previously (*6, 7*). Briefly, samples weighing about 0.3 g were pressed into stainless-steel rings at 10,000 psig to form wafers approximately 1 mm thick and 2.2 cm in diameter. The wafers were contained in a controlled atmosphere Mössbauer cell. Provision was made for heating the samples to the temperatures employed for reduction or other gaseous treatments. The cell was constructed from 304 stainless steel and had beryllium windows 0.025 cm thick. The γ-ray beam was collimated so that it passed only through the sample wafer and the beryllium windows. Blank experiments on the cell with the stainless-steel rings showed no resonance absorption peaks. The Mössbauer spectra were recorded on an Austin Science Associates Mössbauer spectrometer using a ^{57}Co–Cr source driven with constant acceleration. All isomer shifts are reported with respect to this source. The minimum linewidth obtainable with the spectrometer was 0.27 mm/sec, as determined with a sodium nitroprusside absorber containing 8.7×10^{17} ^{57}Fe atoms/cm^2. The isomer shift (δ) and quadrupole splitting (Δ) for the sodium nitroprusside absorber with respect to the ^{57}Co–Cr source were -0.11 and 1.69 mm/sec, respectively, in good agreement with values previously reported in the literature (*8*). The computer methods employed in analyzing the Mössbauer spectra have been described previously (*6, 7*).

Some Mössbauer experiments at low temperatures requiring the use of liquid helium were performed at Stanford University, courtesy of Professor Michel Boudart. The apparatus in Professor Boudart's laboratory has been described in the literature (*9*).

Materials. Alumina-supported iridium, platinum, and platinum–iridium catalysts containing, respectively, 1.75 wt% iridium, 1.75 wt% platinum, and 1.75 wt% each of platinum and iridium were investigated in this work. For the purpose of Mössbauer spectroscopy experiments, each of the catalysts contained an amount of ^{57}Fe enriched iron (0.1 wt%) which was small compared to the amount of platinum and/or iridium present. The ^{57}Fe served as a sensitive Mössbauer probe for the investigation of the state of the platinum and iridium in the catalysts. The catalysts were prepared by impregnating batches of alumina with solutions of appropriate compounds of the metals, using 0.5 ml of solution per gram of alumina. The alumina was obtained from Engelhard Industries in the form of 1/16 in. extrudates (commonly used as a reforming catalyst support). The extrudates were crushed to <200 mesh prior to preparation of the catalysts. The surface area of the alumina was approximately 200 m^2/g. In the preparation of the iridium and platinum catalysts, solutions of chloroiridic and chloroplatinic acids were used in the impregnations. A mixed solution of the two acids was employed in the preparation of the platinum–iridium catalyst. Steps subsequent to impregnation in the preparation of the catalysts included drying in air at 120°C for 16 hr and at 260°C for 4 hr. The Mössbauer probe isotope ^{57}Fe was then incorporated into these materials by impregnating them with a solution prepared by dissolving iron containing 93% of the isotope ^{57}Fe in 6 *N* HNO_3 (*7*). The materials were then dried again for 16 hr at 120°C and 1 hr at 260°C in air. For comparison, a sample containing only ^{57}Fe enriched iron on alumina was prepared in the same manner. Prior to Mössbauer spectroscopy experiments, the samples were reduced *in situ* in flowing hydrogen at 500°C for 1 hr. The sample containing only ^{57}Fe enriched iron on alumina is designated as sample A in this paper. The platinum, iridium, and bimetallic platinum–iridium catalysts containing ^{57}Fe which have been described in this paragraph are designated as samples B, C, and D, respectively. A physical mixture of samples B and C was prepared by tumbling the powders together in a vial and is designated sample B-C. Catalysts prepared in the same manner as samples B, C, and D except for the use of a calcination temperature of 600°C instead of 260°C were also investigated in the present work, and are designated as samples B-600, C-600, and D-600. Two catalyst samples designated B-H_2O and B-Ir were prepared by contacting sample B (platinum–alumina catalyst containing ^{57}Fe) in its finally reduced form with, respectively, water and a chloroiridic acid solution. Subsequent drying and reduction steps were identical to those employed in the preparation of sample B.

RESULTS

Chemisorption Results

The metal catalysts investigated in this work consist of very small metal clusters or crystallites dispersed on alumina. Estimates of metal dispersion, defined as the ratio of surface metal atoms to total metal atoms in the clusters or crystallites, may be obtained from chemisorption data. Hydrogen chemisorption isotherms obtained at room temperature on platinum–iridium, iridium, and platinum catalysts containing ^{57}Fe (samples D, C, and B, respectively) are shown in Fig. 1. The isotherms are approximately linear over the range of pressures employed in obtaining the data. The linear pressure dependence is associated with a weakly bound fraction of the total chemisorption. An estimate of the strongly bound fraction is commonly made by extrapolating the linear part of the isotherm to zero pressure, since saturation with regard to the strongly chemisorbed component is attained at equilibrium pressures very much lower than those corresponding to the measured isotherm. An alternative method of estimating the amount of strongly chemisorbed hydrogen, which was not employed in the present investigation, involves determination of the amount of hydrogen retained on the catalyst after evacuation of the adsorption cell at room temperature (*4*). The evacuation is commonly conducted for a period of 10 min,

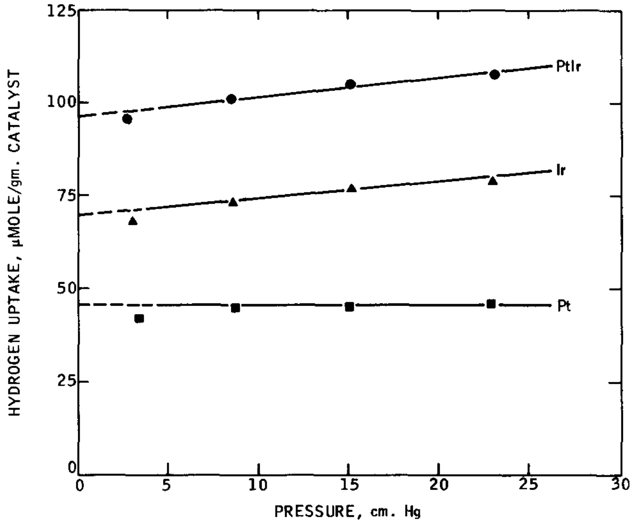

FIG. 1. Hydrogen chemisorption isotherms at room temperature for alumina-supported platinum–iridium, iridium, and platinum (samples D, C, and B, respectively). The platinum–iridium catalyst contained 1.75 wt% each of platinum and iridium, while the other two catalysts contained 1.75 wt% of either platinum or iridium. All of the catalysts were calcined in air at 260°C and reduced in hydrogen at 500°C in their preparation, and contained 0.1 wt% iron (enriched with ^{57}Fe) as a probe for Mössbauer spectroscopy studies.

which results in a final pressure of approximately 10^{-6} Torr. The amount of hydrogen retained is taken as the difference between the original isotherm and a second isotherm determined after the evacuation step. The strongly chemisorbed hydrogen determined in this manner is typically about 75% of the amount determined by extrapolation of the original isotherm to zero pressure.

In Fig. 2 data are shown on the chemisorption of carbon monoxide at room temperature on the same platinum–iridium catalyst for which hydrogen chemisorption data are presented in Fig. 1. Isotherm A is the initial isotherm obtained on the catalyst, while isotherm B is a second isotherm obtained after evacuation of the adsorption cell at room temperature in the manner described in the preceding paragraph. The difference isotherm A − B is the strongly chemisorbed carbon monoxide, which in this case is within about 10% of the amount estimated by extrapolation of isotherm A to zero pressure. The determination of the strongly chemisorbed fraction by the two different methods thus appears to give values in better agreement than is the case for hydrogen chemisorption.

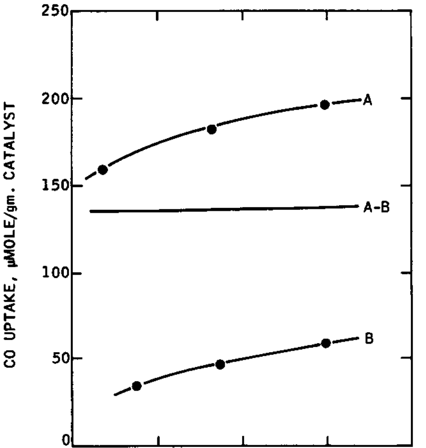

FIG. 2. Chemisorption of carbon monoxide at room temperature on the same platinum–iridium catalyst (sample D) for which hydrogen chemisorption data are presented in Fig. 1. Isotherm A is the original isotherm, while isotherm B is a second isotherm determined after evacuation of the adsorption cell to approximately 10^{-6} Torr subsequent to the completion of isotherm A. The difference isotherm A − B is obtained by subtracting isotherm B from isotherm A, and represents the strongly chemisorbed fraction.

Data were also obtained on the chemisorption of oxygen at room temperature on the catalysts. The results of the experiments on chemisorption of hydrogen, carbon monoxide, and oxygen are summarized in Table 1. The quantities H/M, CO/M, and O/M represent, respectively, the number of hydrogen atoms, carbon monoxide molecules, and oxygen atoms chemisorbed per atom of metal (Pt, Ir, Fe) in the catalyst. The values of H/M and O/M were determined by extrapolation of adsorption isotherms to zero pressure, as illustrated in Fig. 1 for hydrogen. The values of CO/M were determined from difference isotherms of the type labeled A − B in Fig. 2. If we adopt adsorption stoichiometries of one hydrogen or oxygen atom, or one carbon monoxide molecule, per surface metal atom, the values of H/M, CO/M, and O/M provide a direct measure of metal dispersion. We then note some differences in metal dispersion for a given catalyst as determined with the different gases. The values of CO/M are lower than the values of H/M and O/M and may be an indication that part of the chemisorbed carbon monoxide consists of the bridged structure, in which two surface metal atoms are required for each adsorbed molecule. Except for iridium catalyst C, the values of H/M and O/M are nearly equal. The value of H/M in excess of unity for the iridium catalyst is consistent with other observations in hydrogen chemisorption on iridium-containing catalysts (*4*), and suggests that some surface atoms in the metal clusters (perhaps atoms at edges and corners) may adsorb more than one hydrogen atom.

The values of H/M in Table 1, rounded off to the nearest tenth, indicate metal dispersions of 0.9, 1.0, and 1.0, respectively, for the platinum, iridium, and bimetallic platinum–iridium catalysts (samples B, C, D), if we assume that the value in excess of

TABLE 1

Summary of Chemisorption Data on Pt, Ir, and PtIr Catalysts Containing ^{57}Fe

Composition (wt%)[a]	Sample	Air calcination temperature (°C)	H/M[b]	CO/M[b]	O/M[b]
0.1 Fe, 1.75 Pt	B	260	0.86	0.54	0.78
	B-600	600	0.95		0.86
0.1 Fe, 1.75 Ir	C	260	1.29	0.78	0.90
	C-600	600	0.04		0.09
0.1 Fe, 1.75 Pt, 1.75 Ir	D	260	1.00	0.68	0.90
	D-600	600	0.57		0.56

[a] The catalysts all consist of metal clusters or crystallites supported on alumina and contain 0.1 wt% Fe (enriched with ^{57}Fe) in addition to the platinum and/or iridium. The ^{57}Fe is present as a probe for Mössbauer spectroscopy experiments. The catalysts were all reduced in H_2 at 500°C and evacuated at 450°C prior to chemisorption measurements at room temperature.

[b] The quantities H/M, CO/M, and O/M represent, respectively, the number of hydrogen atoms, carbon monoxide molecules, and oxygen atoms chemisorbed at room temperature per atom of metal M (Pt, Ir, Fe) in the catalyst. The values of H/M and O/M were determined by extrapolation of the linear regions of the adsorption isotherms to zero pressure, as illustrated in Fig. 1. The values of CO/M were determined from difference isotherms of the type labeled A-B in Fig. 2, and represent the amounts retained after the adsorption cell is evacuated at room temperature for 10 min to approximately 10^{-6} Torr subsequent to completion of the initial isotherm.

unity for the iridium catalyst is indicative of a dispersion of 1.0. If we also consider the carbon monoxide and oxygen chemisorption data, we obtain a measure of the degree of uncertainty in specifying the metal dispersion. If a range of values is used to characterize the metal dispersion of each of the catalysts, the platinum–iridium catalyst calcined at 260°C (sample D) has a metal dispersion in the approximate range of 0.7–1.0. Similarly, the platinum and iridium catalysts calcined at 260C (samples B and C) have metal dispersions in the approximate ranges of, respectively, 0.5–0.9 and 0.8–1.0. Increasing the calcination temperature from 260 to 600C in the preparation of the platinum catalyst (see data on sample B-600) appears to have little effect on the metal dispersion and may actually increase the dispersion slightly. In marked contrast, a similar increase in calcination temperature in the case of the iridium and platinum–iridium catalysts (see data on samples C-600 and D-600, respectively) results in a marked decrease in metal dispersion. In the case of iridium-containing catalysts, the loss of metal dispersion is due to oxidation and agglomeration of the iridium, with the formation of large crystallites of IrO_2. This has been demonstrated clearly by X-ray diffraction data (*2*, *4*). On subsequent reduction, the catalysts exhibit large crystallites of iridium. The dispersion of the iridium catalyst decreases by at least an order of magnitude when the calcination temperature is increased from 260 to 600°C. In the case of the platinum–iridium catalyst, the decrease in total metal dispersion is less pronounced since the platinum in the catalyst remains highly dispersed.

Mössbauer Spectroscopy Results

As indicated earlier in the paper, each of the catalysts in this investigation contained a small amount of iron (0.1 wt%) enriched with the Mössbauer isotope ^{57}Fe. The Mössbauer resonance is sensitive to the environment of the ^{57}Fe nuclei in the catalyst, and hence the ^{57}Fe serves as a probe to provide information on the catalyst. Spectra for various catalyst samples of interest in this investigation are shown in Figs. 3, 4, 5, and 6. Parameters associated with the Mössbauer resonance were derived from

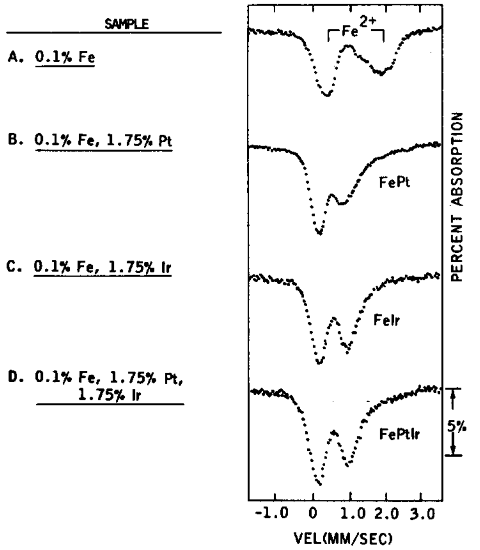

FIG. 3. Mössbauer spectra at 25°C on alumina-supported platinum–iridium, iridium, and platinum catalysts containing a small amount of Fe (0.1 wt%) enriched with ^{57}Fe as a Mössbauer probe. The catalysts (samples B, C, D) are the same as those for which hydrogen chemisorption data are presented in Fig. 1. The Mössbauer spectrum on the alumina-supported iron sample (sample A) containing 0.1 wt% Fe enriched with ^{57}Fe serves as a reference for comparison with the spectra on the catalysts.

the spectra by a computerized data analysis procedure which has been described previously (*6*). Values of Mössbauer parameters of the ^{57}Fe derived from room temperature spectra on the various supported catalysts containing platinum and/or iridium and on a sample of alumina containing only the iron are summarized in Table 2. In the determination of the parameters in Table 2 the Mössbauer spectra, i.e., the spectra of Figs. 3, 5, and 6, were treated as two line spectra. The parameters include the isomer shift δ, the quadrupole splitting Δ, and the ratios of the areas (A_2/A_1) and widths (W_2/W_1) of the two lines in the spectra.

Mössbauer spectra at 25°C are shown in Fig. 3 for alumina-supported platinum, iridium, and bimetallic platinum–iridium catalysts containing ^{57}Fe (samples B, C, and D, respectively) and for alumina containing only the iron (sample A). A spectrum (not shown in Fig. 3) was also obtained on sample B-C, a physical mixture of samples B and C. The two line (quadrupole split) spectrum for sample A and the corresponding Mössbauer parameters for this sample in Table 2 are characteristic of high spin ferrous ions in oxides (*7*), which indicates that the iron in the sample is reduced only to the ferrous state with hydrogen at 500°C. There is no evidence for the presence of iron in the metallic state. The large linewidths and the differences in intensity of the lines suggest that the iron has a number of different environments. The spectra from samples B, C, and D in Fig. 3 are very different from that for sample A. Correspondingly, the Mössbauer parameters in Table 2 for samples B, C, D, and B-C contrast markedly with those for sample A. These results are indicative of differences in the chemical environment of the iron. The presence of platinum and/or iridium leads to a marked decrease in the amount of iron which exists as ferrous ions in the samples. The iron is therefore present in a different chemical state which is characterized by an intimate association with highly dispersed clusters of platinum and/or iridium. The evidence for association of the iron atoms with platinum in samples similar to B has been discussed previously in some detail (*10*). Briefly, incorporation of iron atoms into the platinum clusters is indicated by the agreement of the isomer shift for iron in the catalyst with that for iron in a PtFe bulk alloy of similar composition. In addition, it was found that the iron in sample B, after reduction at 500°C, exhibited a unique chemical behavior in that it could be reversibly oxidized and reduced at room temperature. This property appears to be characteristic of iron in association with metals such as platinum and palladium (*6, 7, 9, 10*). It is not observed when the iron is present by itself on alumina. Sample C containing iridium and iron exhibited the same reversible oxidation–reduction behavior indicating the incorporation of the iron into the iridium clusters. The isomer shift for sample

TABLE 2

Summary of Mössbauer Parameters for Reduced Pt, Ir, and PtIr Catalysts Containing ^{57}Fe

Composition (wt%)[a]	Sample[b]	Isomer shift δ (mm/sec)	Quadrupole splitting (mm/sec)	A_2/A_1[c]	W_2/W_1[c]
0.1 Fe	A	1.20	1.69	1.01	1.32
0.1 Fe, 1.75 Pt	B	0.53	0.82	1.71	2.41
	B-600	0.55	0.86	1.90	2.73
	B-H_2O[d]	0.53	0.83	1.71	2.38
0.1 Fe, 1.75 Ir	C	0.58	0.97	1.18	1.58
	C-600	1.22	1.86	0.98	1.38
0.1 Fe, 1.75 Pt, 1.75 Ir	D	0.56	0.89	1.16	1.38
	D-600	0.57	0.92	1.50	2.16
	B-Ir[d]	0.57	0.86	1.13	1.40
0.1 Fe, 1.75 Pt mixed with 0.1 Fe, 1.75 Ir	B-C[e]	0.57	0.92	1.28	1.79

[a] The concentrations of metallic components of interest, expressed as wt% of the total mass of material, which includes the metallic elements shown and the alumina carrier. The ^{57}Fe fraction of the 0.1 wt% Fe present in all cases serves as a Mössbauer probe of the catalyst. The composition listed as 0.1 Fe (sample A) is a reference material in which Fe is dispersed on alumina with no platinum or iridium present.

[b] Samples A, B, B-H_2O, C, D, and B-Ir were all calcined in air at 260°C in their preparation, while samples B-600, C-600, and D-600 were calcined at 600°C.

[c] The ratios of the areas (A_2/A_1) and widths (W_2/W_1) of the two lines in the Mössbauer spectra in Figs. 3, 5, and 6. The subscript 1 refers to the line corresponding to the lower Doppler velocity.

[d] Catalyst samples prepared by contacting sample B in its finally reduced form with water (designated B-H_2O) or with a chloroiridic acid solution (designated B-Ir), followed by drying and reduction steps identical to those employed in the preparation of the original sample B.

[e] Physical mixture of equal portions of samples B and C.

C, however, was not in good agreement with the value of 0.38 mm $\sec^{-1}$ (*8*) expected for dilute iron in iridium alloys. This difference may reflect an unusual chemical state for iron which is associated with surface iridium atoms in clusters. A similar situation has recently been reported and discussed for iron–ruthenium catalysts (*11*).

The Mössbauer parameters for sample D differ from those for samples B and C, which indicates that the iron atoms in sample D are not associated exclusively with either the platinum or the iridium in the catalyst. Furthermore, the area and linewidth ratios (A_2/A_1 and W_2/W_1) for sample D differ from those for the physical mixture B-C, which indicates that the iron atoms in sample D are not simply distributed between platinum clusters and iridium clusters with the platinum and iridium being totally isolated from each other. The data on Mössbauer parameters are consistent with the view that catalyst D consists of bimetallic platinum–iridium clusters with iron atoms incorporated therein.

Mössbauer spectra obtained at very low temperatures (18–23.5°K) on samples B, C, and D are shown in Fig. 4. At these temperatures the samples become ferromagnetic and the spectra exhibit magnetic hyperfine splitting. As a result, the spectra consist of six lines instead of two. While the six lines in the spectra of Fig. 4 are not very pronounced, they are nonetheless real, as demonstrated by the computer analysis of the data. The positions of the lines from this analysis are shown above the spectra in Fig. 4. The magnitude of the magnetic field experienced by the ^{57}Fe nuclei can be determined from the separation of lines in the spectrum (*12*, *13*). Magnetic fields derived

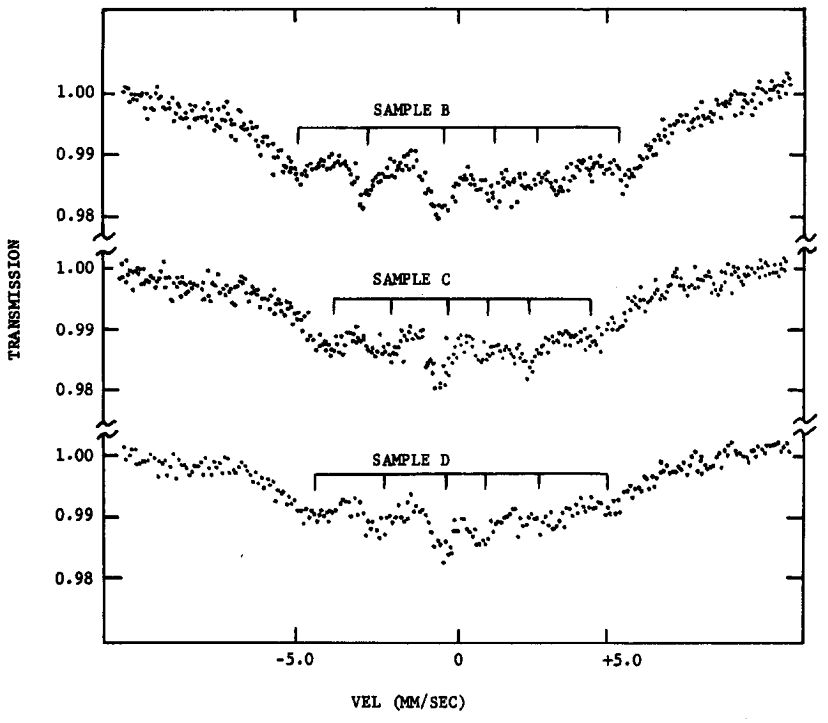

FIG. 4. Low temperature (18–23.5°K) Mössbauer spectroscopy data on the same catalysts (samples B, C, D) used in obtaining the room temperature Mössbauer spectroscopy data in Fig. 3. The data exhibit magnetic hyperfine splitting because of the ferromagnetic character of the samples at the low temperatures. The splitting leads to spectra consisting of six lines. The magnitude of the splitting varies for the different catalysts, indicating differences in the local magnetic fields at the ^{57}Fe nuclei. The positions of the six lines determined by computer analysis of the data are shown above each of the spectra.

from the separation of the outermost of the six lines of the hyperfine spectra in Fig. 4 are given in Table 3. Since the internal magnetic field is different for each of the three samples, which differ with regard to the metal or metals (platinum and/or iridium) present, the results provide additional evidence that the iron atoms are associated with these metals. In studies on bulk PtFe, IrFe, and PtIrFe alloys, it has been observed (*14*, *15*) that the magnetic fields at the iron nuclei are much smaller for IrFe than for PtFe. In addition, these studies showed that the magnetic fields for PtIrFe alloys were intermediate between those for PtFe and IrFe alloys. The same trend is found with samples B, C, and D in Table 3, which is consistent with the view that the iron atoms in sample D are incorporated in bimetallic clusters of platinum and iridium. It is of interest to note that the magnetic field at the ^{57}Fe nuclei in the platinum catalyst (sample B) is similar to that reported for highly dispersed PtFe alloys on carbon (*9*) and for bulk PtFe alloys (*15*). However, the fields at the ^{57}Fe nuclei in the iridium and platinum–iridium catalysts (samples C and D) are much larger than

TABLE 3

Magnetic Fields Derived from Magnetic Hyperfine Structure

Sample and composition (wt %)	Temperature (°K)	Magnetic field (koe)
B (0.1 Fe, 1.75 Pt)	21	325
C (0.1 Fe, 1.75 Ir)	23.5	260
D (0.1 Fe, 1.75 Pt, 1.75 Ir)	18	295

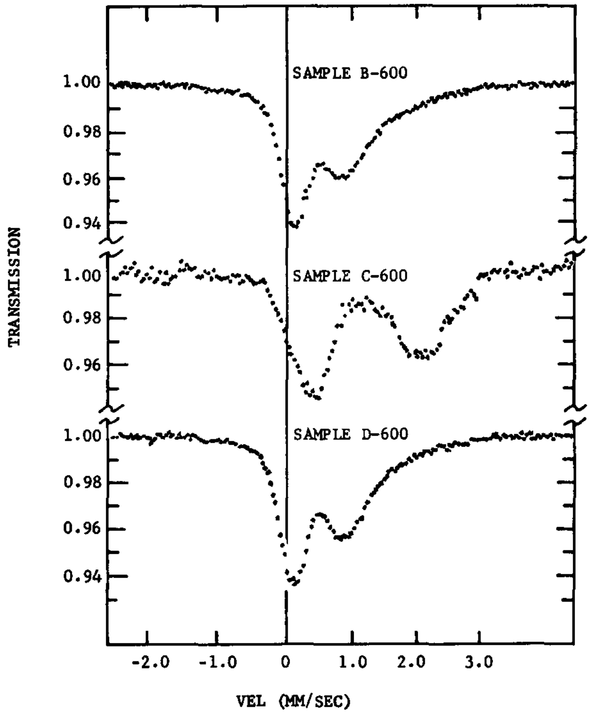

FIG. 5. Mössbauer spectra at 25°C on alumina-supported platinum–iridium, iridium, and platinum catalysts which were calcined in air at a temperature of 600°C in their preparation (samples D-600, C-600, and B-600, respectively). The catalysts have the same elemental compositions as the catalysts for which Mössbauer spectra are shown in Fig. 3, but exhibit structural differences due to the higher calcination temperature (600 vs 260°C) employed in their preparation.

those observed with bulk IrFe and PtIrFe alloys (*14*, *15*). The data thus indicate a strong effect of the degree of metal dispersion on the magnetic properties of the IrFe and PtIrFe systems which is not observed with the PtFe system.

In the preparation of iridium-containing catalysts, the temperature of calcination in air is critical, as was noted in the previous section on chemisorption results. Mössbauer spectra at 25°C are shown in Fig. 5 for platinum, iridium, and bimetallic platinum–iridium catalysts (samples B-600, C-600, and D-600, respectively) which were prepared by calcination in air at 600°C prior to the final reduction in hydrogen at 500°C. Sample B-600 gives a spectrum similar to that of sample B in Fig. 3, and the Mössbauer parameters for these samples in Table 2 are also similar. These results indicate that sample B-600 also consists of platinum clusters with iron atoms incorporated therein. However, sample C-600 gives a spectrum which is very different from that presented for sample C in Fig. 3. The spectrum for sample C-600 is nearly identical to that of sample A in Fig. 3, in which the iron exists in the ferrous state. The iridium in sample C-600 is not present as highly dispersed clusters, as can be seen from the chemisorption data in Table 1. We conclude that the poorly dispersed iridium crystallites (dispersion <0.1) are not associated to a significant extent with the iron in the sample. Hence sample C-600 behaves like a sample containing no iridium. The Mössbauer parameters in Table 2 are consistent with this statement. The spectrum of sample D-600 resembles that of sample B in Fig. 3 more closely than it resembles the spectrum of sample D. The Mössbauer parameters in Table 2, especially the ratios

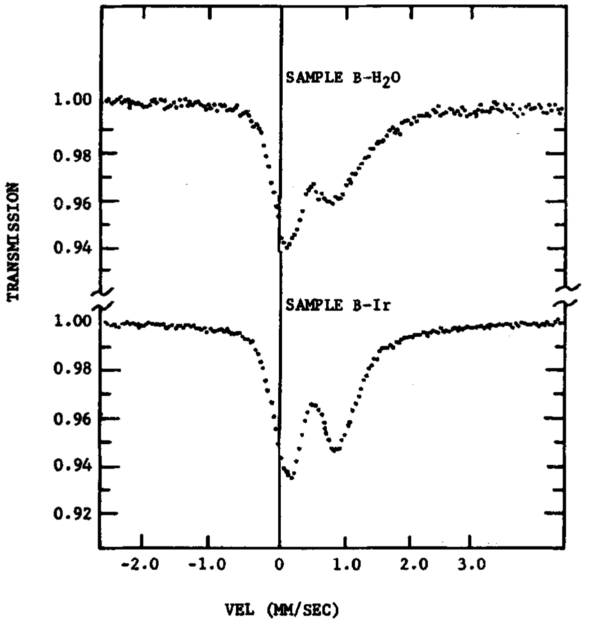

FIG. 6. Mössbauer spectra at 25°C on catalyst samples B-H_2O and B-Ir prepared by contacting platinum–alumina catalyst (sample B of Figs. 1, 3, and 4) in its final reduced form with, respectively, water and a chloroiridic acid solution. The subsequent drying and reduction steps in the preparation of samples B-H_2O and B-Ir were identical to those employed in the preparation of sample B. The platinum and iridium contents of sample B-Ir are the same as those of sample D.

A_2/A_1 and W_2/W_1, show evidence of differences between samples D and D-600. The iridium in sample D-600 is largely present in the same poorly dispersed form as the iridium in sample C-600, as has been found from X-ray diffraction studies of similar samples. Sample D-600 thus can be characterized approximately as consisting of highly dispersed platinum clusters incorporating iron atoms and separate iridium crystallites of much lower dispersion which are not associated with iron atoms to a significant extent. This characterization is consistent with the chemisorption data in Table 1. The Mössbauer data on sample D-600, coupled with the chemisorption data on this sample in Table 1, show that calcination of alumina supported platinum–iridium in air at 600°C is unsatisfactory for the formation of highly dispersed bimetallic clusters of platinum and iridium.

Mössbauer spectroscopy data on an alumina-supported platinum–iridium sample prepared by a sequential impregnation procedure are of interest in providing information on the tendency of platinum and iridium to form bimetallic clusters. As indicated in the experimental section of this paper, the sample was prepared by contacting the platinum–alumina catalyst containing ^{57}Fe (sample B) with a chloroiridic acid solution after the hydrogen reduction step. On the basis of the evidence presented earlier, the sample, prior to contact with the chloroiridic acid solution, may be characterized as containing highly dispersed platinum clusters with iron atoms incorporated therein. After drying and reduction steps identical to those employed in the preparation of samples B, C, and D, the resulting material (designated as sample B-Ir) had the same elemental composition as sample D. Another sample prepared in exactly the same manner, except that water was substituted for the chloroiridic acid solution, served as a reference material (designated as sample B-H_2O). Mössbauer spectra at 25°C on these samples are presented in Fig. 6. The spectrum and Mössbauer parameters of sample B-H_2O are similar to those of sample B (Fig. 3 and Table 2). Sample B is therefore unaffected by its treatment with water. The spectrum of sample B-Ir is similar to that of sample D in Fig. 3, and the Mössbauer parameters in Table 2 are also similar. The data indicate that platinum clusters associated with iron are altered by addition of iridium to the sample. We conclude that the added iridium is incorporated in the platinum clusters to give PtIr clusters containing the iron probe atoms. If the added iridium was present as separate iridium clusters in sample B-Ir, the Mössbauer spectrum should have been the same as that of sample B-H_2O or sample B. These results provide a good illustration of the propensity of platinum and iridium atoms to mix and form bimetallic clusters, rather than to form monometallic clusters consisting exclusively of atoms of one or the other of the two metals.

DISCUSSION

Evidence for the presence of bimetallic clusters of platinum and iridium dispersed on silica has previously been obtained by X-ray diffraction studies for catalysts in which about one-fourth to one-half of the total number of platinum and iridium atoms are present in the surface of the clusters (*2, 4*). However, it becomes very difficult to extend the studies to catalysts with metal dispersions approaching unity. The lines in the diffraction pattern are very broad and weak in such highly dispersed catalysts, and become indistinguishable from the background. Furthermore, alumina-supported platinum–iridium catalysts have the additional complication that the diffraction pattern of the alumina interferes with that of the platinum–iridium clusters. In view of these considerations, the investigation of a highly dispersed, alumina-supported platinum–iridium catalyst by Mössbauer spectroscopy is of particular interest. The work complements the earlier X-ray diffraction studies on silica-supported platinum–iridium catalysts.

The approach of adding a small amount of the Mössbauer isotope ^{57}Fe as a probe to investigate the nature of the platinum and iridium in the catalyst has been found to be very useful. Previous studies of alumina-supported palladium and platinum catalysts to which a small amount of ^{57}Fe was added provided good evidence that the iron was intimately associated with the palladium or platinum in the catalyst (*6, 7, 10*). This finding has been corroborated for the platinum- and iridium-containing catalysts of the present investigation and serves to validate the use of ^{57}Fe as a probe. In the present work we are concerned with the additional matter of distinguishing iron associated with platinum clusters from iron associated with iridium clusters, and more importantly with distinguishing either of these from a situation in which iron is associated with atoms of both platinum and iridium in a bimetallic cluster. The Mössbauer parameters in Table 2 derived from spectra at 25°C and the hyperfine magnetic fields in Table 3 derived from the hyperfine splittings in the low-temperature spectra clearly distinguish the situation in which iron is associated with platinum from one in which it is associated with iridium. In the respect that parameters such as the isomer shift, the quadrupole splitting, and the hyperfine magnetic field for the platinum–iridium catalyst calcined at 260°C are intermediate between the values for the platinum and iridium catalysts calcined at the same temperature, it seems reasonable to state that the data are consistent with the existence of bimetallic platinum–iridium clusters in the former. The possibility that the spectra and Mössbauer parameters for the platinum–iridium catalyst reflect an average of contributions from separate platinum and iridium clusters, each of which has ^{57}Fe atoms incorporated therein, must be considered. The fact that the area and linewidth ratios (A_2/A_1 and W_2/W_1) for the

Mössbauer spectrum on the physical mixture of platinum plus ^{57}Fe on alumina and iridium plus ^{57}Fe on alumina (sample B-C) are significantly different from those of the bimetallic platinum–iridium catalyst containing ^{57}Fe (sample D) argues against this possibility. Close examination of all aspects of the data favors the existence of bimetallic platinum–iridium clusters. The data on the platinum–iridium catalyst prepared by sequential impregnation are perhaps more convincing in this regard. In this experiment a platinum catalyst in which ^{57}Fe atoms are intimately associated with the platinum clusters is contacted with chloroiridic acid to incorporate iridium in the catalyst. After the resulting material is dried and reduced, a Mössbauer spectrum of the ^{57}Fe in the final material is different from what it was in the original platinum catalyst and nearly identical to that of the ^{57}Fe in the platinum–iridium catalyst prepared by coimpregnation. This is verified by the Mössbauer parameters in Table 2, thus providing evidence of effective interaction between the original platinum clusters containing ^{57}Fe atoms and the added iridium. The formation of bimetallic platinum–iridium clusters on contact of the iridium with the platinum catalyst is therefore indicated. If there were no interaction between the platinum and iridium, the spectrum and parameters would not have changed; i.e., they would have been identical to the spectrum and parameters for the original platinum catalyst. The preparation of a platinum–iridium catalyst by coimpregnation of alumina with chloroplatinic and chloroiridic acids should be at least as favorable for interaction between platinum and iridium as a preparation involving a sequential procedure of the type just described. Therefore, we conclude that bimetallic platinum–iridium clusters will normally exist in either type of preparation, if the temperature of exposure of the catalyst to air during its preparation is not too high. In general, the catalyst may be exposed to air at temperatures lower than about 375°C without harm, but exposure to air at temperatures higher than about 450°C should be avoided (*2*, *4*).

When the temperature of exposure of platinum–iridium catalysts to air is too high, either in their original preparation or in subsequent use, the iridium undergoes oxidation and agglomeration to form large crystallites of IrO_2. X-ray diffraction data on platinum–iridium–silica and platinum–iridium–alumina catalysts calcined in air at 500°C show IrO_2 crystallites with sizes of 290 and 260 Å, respectively (*2*, *4*). On subsequent reduction in hydrogen, the catalysts may be characterized approximately as systems containing two different types of metallic entities, one consisting of highly dispersed platinum or platinum-rich clusters and the other consisting of large iridium or iridium-rich crystallites. The Mössbauer spectroscopy data on platinum–iridium catalysts calcined in air at 600°C in their preparation are entirely in accord with this picture.

To summarize briefly, the Mössbauer spectroscopy results in the present paper provide evidence for bimetallic platinum–iridium clusters in catalysts in which virtually all of the platinum and iridium atoms are surface atoms. These results, in conjunction with chemisorption results and X-ray diffraction data, have provided an effective characterization of platinum–iridium catalysts over a wide range of metal dispersions.

ACKNOWLEDGMENTS

The authors thank H. W. Dougherty and L. W. Turaew for their expert technical assistance in conducting many of the experiments reported in this paper. Special thanks go to James A. Dumesic and other members of the Laboratory for the Study of Adsorption and Catalysis at Stanford University for assistance in the Mössbauer experiments at liquid helium temperature.

REFERENCES

1. Sinfelt, J. H., *J. Catal.* **29,** 308 (1973).
2. 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.

3. Sinfelt, J. H., *Accounts Chem. Res.* **10,** 15 (1977).
4. Sinfelt, J. H., and Via, G. H., *J. Catal.* **56,** 1 (1979).
5. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8,** 82 (1967).
6. Garten, R. L., and Ollis, D. F., *J. Catal.* **35,** 232 (1974).
7. Garten, R. L., *J. Catal.* **43,** 18 (1976).
8. Stevens, J. G., and Stevens, V. E., "Mössbauer Effect Data Index," p. 156, Plenum, New York, 1973.
9. Bartholomew, C. H., and Boudart, M., *J. Catal.* **29,** 278 (1973).
10. Vannice, M. A., and Garten, R. L., *J. Molec. Catal.* **1,** 201 (1975/76).
11. Vannice, M. A., Lam, Y. L., and Garten, R. L., *Preprints, ACS Div. Petr. Chem.* **23,** 495 (1978).
12. Frauenfelder, H., "The Mössbauer Effect," pp. 51–53, 82, 83, Benjamin, New York, 1962.
13. Wertheim, G. K., *J. Appl. Phys.* (*Suppl.*) **32,** 110S (1961).
14. Mizoguchi, T., Sasaki, T., and Chikazumi, S., *Amer. Inst. Phys. Conf. Proc.* **5,** 445 (1972).
15. Kanashiro, M., and Kunitomi, N., *J. Phys. Soc. Japan* **43,** 1559 (1977).