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Direct Evidence for Bimetallic Clusters

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Direct evidence for the formation of bimetallic clusters as proposed by Sinfelt is obtained from Mössbauer spectroscopic studies of Fe and PdFe/η-Al_2O_3 catalysts. Mössbauer spectroscopy was used to determine the chemical states of iron on η-Al_2O_3 in the absence and presence of palladium for various reduction and oxidation treatments.

Ferric ions on η-Al_2O_3 in low concentrations (0.1%) were unaffected by H_2 or CO at room temperature and were reduced only to the ferrous state in H_2 at 973°K or below. In PdFe/η-Al_2O_3 catalysts, however, the iron is reduced at room temperature to the ferrous state in H_2 or CO providing evidence that the iron and palladium were already associated in the catalyst as prepared. Reduction of PdFe/η-Al_2O_3 at 673°K gave a catalyst with 54% dispersion and Mössbauer parameters consistent with well-dispersed PdFe bimetallic clusters. The iron in this material could be reversibly oxidized in O_2 and reduced in H_2 at room temperature—a characteristic which we attribute to iron associated with palladium. Agglomeration of PdFe/η-Al_2O_3 in H_2 at successively higher temperatures up to 973°K caused a fivefold decrease in dispersion from 54 to 11%. At the same time the quadrupole split Mössbauer spectrum characteristic of iron at the surface of well-dispersed PdFe clusters collapsed into a broad single line characteristic of iron "in" the agglomerated PdFe clusters. With decreasing dispersion the amount of iron which could be oxidized to the ferric state on exposing the reduced catalysts to O_2 at room temperature also decreased and "surface" and "bulk" peaks for the clusters could be resolved.

The Mössbauer parameters, chemical behavior and changes in Mössbauer spectra of PdFe/η-Al_2O_3 catalysts on agglomeration provide conclusive evidence that bimetallic clusters are formed in catalysts prepared by the usual impregnation, drying and calcination techniques.

INTRODUCTION

The recent discovery and successful development of supported multicomponent catalysts for catalytic reforming has stimulated renewed interest in catalysis by alloys from both the fundamental and practical points of view. Fundamental investigations aimed at determining the relationship between the chemical structure and catalytic properties of alloys usually employ bulk metals since alloy formation can be verified by X-ray diffraction analysis (*1*) and surface composition can be examined by Auger spectroscopy (*2*), work function measurements (*3*) and chemisorption techniques (*1*, *4*). Studies of the bulk metals have clearly established that alloying can dramatically alter catalytic and chemisorption properties (*1*, *5*).

Supported multicomponent catalysts are of greater practical interest than bulk alloys but are much less amenable to characterization and fundamental understanding. This results from the fact that the supported components are typically present in small concentrations with particle diameters in the 1–5 nm range. For such materials, structural and chemical information on the dispersed components are difficult to obtain by physical tools which have been applied to bulk metals.

Chemisorption and catalytic probes have been the primary means for investigating the question of "alloying" in supported multicomponent catalysts. Sinfelt (*6*), for example, has recently shown that the chemisorption and catalytic properties of silica-supported RuCu and OsCu catalysts cannot be explained by simply adding the catalytic activities of the individual metals. He proposed that in these bimetallic catalysts the metals formed well-dispersed bimetallic clusters which are a mixture of the metals on an atomic scale.

Direct confirmation of the existence of bimetallic clusters in supported catalysts requires that the chemical state or local environment of at least one of the components be determined. Mössbauer spectroscopy, although easily applicable to only a limited number of elements, has the advantage of providing chemical information regardless of the state of dispersion or degree of ordering of a solid. This technique is thus particularly suited for the investigation of "real" catalysts in cases where it is applicable.

In this investigation we have applied the Mössbauer technique to investigate the question of bimetallic clusters in PdFe/η-Al_2O_3. The approach adopted here was to determine the chemical states of iron on Al_2O_3 in the presence and absence of palladium for various treatments. On the basis of Mössbauer parameters, dispersion measurements and the chemical behavior of iron in PdFe catalysts firm evidence for bimetallic clusters was obtained.

EXPERIMENTAL METHODS

An η-Al_2O_3 support prepared by calcining Davison β-trihydrate of alumina for 4 hr in air at 863°K was used in this investigation. The surface area of the support was 245 m^2 g^{-1}. The catalysts were prepared by impregnating alumina with metal solutions of appropriate concentrations in a ratio of 0.5 cm^3 solution/g of support. The metal solutions were added to the support a few drops at a time with thorough mixing between additions. The impregnated catalysts were then dried and calcined by a *standard calcination treatment*. This treatment consisted of an overnight drying in air at 393°K followed by a 3 hr calcination in air at 773°K.

TABLE 1

Description of η-Al_2O_3 Supported Catalysts

Catalyst	Fe (%)	Pd (%)	Pd/Fe Ratio
A	0.1		—
B	0.1	0.52	2.7
C	0.1	2.2	11.6
D	0.1	4.75	24.9
E	0.1 (physical mixture)	4.75	24.9

The palladium solution was prepared by dissolving $PdCl_2$ (Engelhard Industries, Inc., Newark, N.J.) in concentrated HCl. The HCl solution was subsequently evaporated to near dryness twice and diluted with distilled water after each evaporation. The pH of the final solution was ~3. The iron solution was prepared from Fe_2O_3 93% isotopically enriched in ^{57}Fe. The enriched Fe_2O_3 was obtained from Oak Ridge National Laboratories, Oak Ridge, Tenn. The Fe_2O_3 was reduced 2 hr in hydrogen at 723°K and dissolved in 6 N HNO_3. The HNO_3 solution was evaporated to near dryness twice and diluted each time with distilled water. The pH of the final solution was ~1.

The catalysts employed in this investigation are described in Table 1. Samples B–E were impregnated sequentially with palladium and then iron. After each impregnation the sample was given the standard calcination treatment. Sample E was a physical mixture of two catalysts—0.2% Fe/η-Al_2O_3 and 9.5% Pd/η-Al_2O_3. Each catalyst was separately given the standard calcination treatment. The catalysts were then mixed in a ball-mill for 16 hr.

Hydrogen of 99.95% initial purity was used in all reductions and was further purified by a Deoxo unit followed by a 5A molecular sieve drying trap. Oxygen of 99.5% purity was used without further urification.

Apparatus and Procedure

For the Mössbauer experiments catalyst samples weighing ~0.3 g were pressed into stainless steel rings at 10,000 psig to form wafers ~1 mm thick and 2.2 cm in diameter. The wafers were placed in a controlled temperature and atmosphere Mössbauer cell. The cell was constructed from 304 stainless steel and had 0.025 cm thick beryllium windows. The gamma ray beam was collimated so that it passed only through the catalyst wafer and the beryllium windows. Blank experiments on the cell with the stainless steel rings but no catalyst in place showed no resonance absorption peaks. The catalyst samples were heated by an external heater and the temperature was measured by an internal thermocouple located near the sample wafer.

The Mössbauer spectra were recorded on an Austin Science Associates Mössbauer spectrometer using a ^{57}Co–Cr source. All isomer shifts are reported with respect to that source. The minimum linewidth obtainable with the spectrometer was 0.27 mm sec^{-1} as determined with a sodium nitroprusside absorber containing 8.7×10^{17} Fe 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^{-1}, respectively, in good agreement with values reported in the literature (*7*). The source was driven with constant acceleration and was slaved to an asymmetric wave form (flyback mode) so that a single spectrum was recorded by an ND 2200 multichannel analyzer (MCA). Velocity calibration was obtained for every other channel of the MCA by interferometry (*8*).

Methods used to computer analyze the Mössbauer spectra have been described previously (*9*). Spectral areas were computed from the parameters determined by computer analysis and were corrected for background radiation using the method of Housley *et al.* (*10*).

The dispersion of the palladium catalysts was determined by hydrogen chemisorption on a conventional volumetric apparatus following the method of Aben (*11*). Pressure measurements were made with a Texas Instruments precision gauge. In Aben's method the hydrogen monolayer coverage of palladium is determined at 1 mm Hg hydrogen pressure and 343°K. Under these conditions hydrogen absorption is insignificant amounting to 0.002 hydrogen atoms/palladium atom. For the dispersion measurements the PdFe/Al_2O_3 catalysts were reduced at temperatures from 673–973°K, cooled to 673°K in flowing hydrogen and evacuated for 2 hr at 673°K. The sample was then cooled to 343°K while the evacuation was continued and then the hydrogen adsorption was determined. Increasing the evacuation time at 673°K to 12 hr had no effect on the dispersion measurements.

RESULTS

The effect of palladium on the chemical states of iron in alumina-supported catalysts was first investigated for a series of samples containing 0.1 wt% Fe and varying amounts of palladium. All catalysts were prepared and calcined in the same manner to allow comparison of the data from the different samples. Each catalyst was subjected to an identical series of treatments and the chemical state of the iron was followed by Mössbauer spectroscopy. Finally, Cat. D (0.1% Fe, 4.75% Pd/η-Al_2O_3) was investigated in detail to provide a better understanding of the chemical nature of the iron in PdFe/Al_2O_3 catalysts. Unless otherwise noted, all spectra were recorded at 298 ± 2°K in 1 atm of the gas used in a particular treatment.

The Effect of Pd Concentration on the Mössbauer Spectra of 0.1% Fe/η-Al_2O_3

The Mössbauer spectra of Cat. A–E were compared after reduction of each sample for 1 hr at 673°K and after reduction for 2 hr at 973°K. The results of these studies are shown in Figs. 1 and 2.

For Cat. A (0.1% Fe/η-Al_2O_3) both reduction temperatures gave quadrupole split spectra similar to those reported previously for 0.05% Fe/η-Al_2O_3 (*9*). The large linewidths and intensity differences in the absorption peaks suggest that a multiplicity of iron environments were present. Computer analysis of Figs. 1A and 2A for two peaks gave the Mössbauer parameters shown in Table 2. These parameters are typical of high spin ferrous ions in oxides and show that Cat. A can only be reduced to the ferrous state even at 973°K. More detailed computer analyses of Figs. 1A and B with four peaks, i.e., two ferrous doublets, markedly improved the fits to the data.

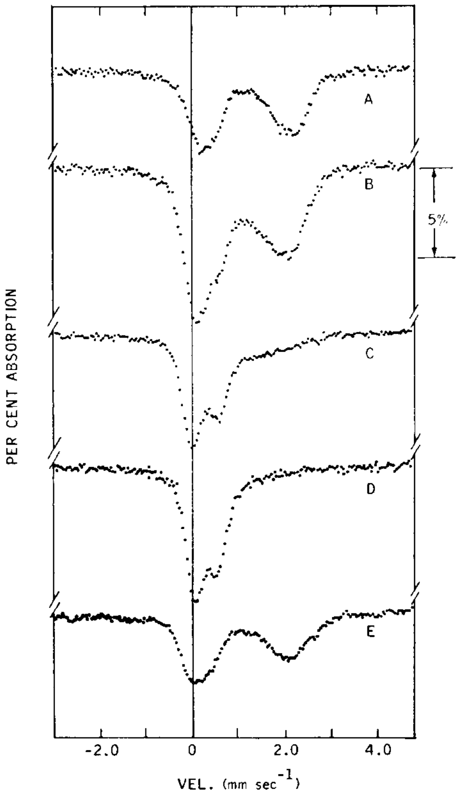

FIG. 1. Mössbauer spectra of Catalysts A–E after reduction for 1 hr in H_2 at 673°K. All catalysts contain 0.1% Fe and are supported on η-Al_2O_3. (A) No Pd; (B) 0.52% Pd; (C) 2.2% Pd; (D) 4.75% Pd; (E) 4.75% Pd, physical mixture. All spectra recorded at 298°K in 1 atm H_2.

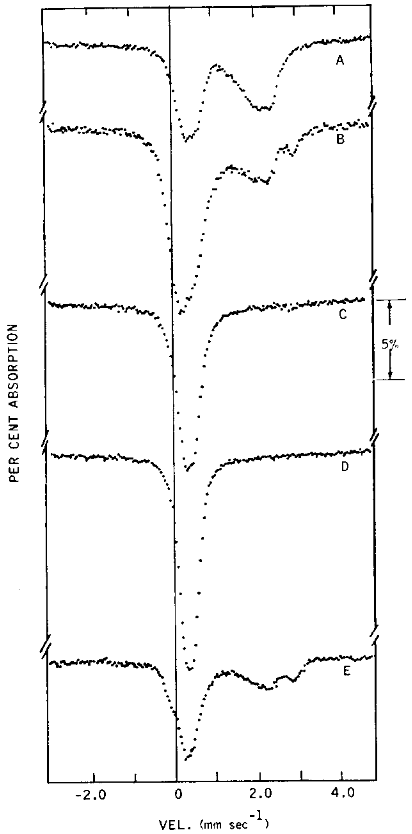

FIG. 2. Mössbauer spectra of Catalysts A–E after reduction for 2 hr in H_2 at 973°K. All catalysts contain 0.1% Fe and are supported on η-Al_2O_3. (A) No Pd; (B) 0.52% Pd; (C) 2.2% Pd; (D) 4.75% Pd; (E) 4.75% Pd, physical mixture. All spectra recorded at 298°K in 1 atm H_2.

The results of such an analysis were similar to those obtained in previous work on a 0.05% Fe/η-Al_2O_3 sample and are discussed in Ref. (*9*).

Figures 1B–E and 2B–E show the effect of palladium loading on the Mössbauer spectra of 0.1% Fe/η-Al_2O_3. It is apparent that palladium markedly altered the chemical nature of the iron. At both temperatures

TABLE 2

Mössbauer Parameters for Reduced Catalyst A

Fig.	Reduction temp (°K)	δ (mm sec^{-1})	Δ (mm sec^{-1})	χ^2
1A	673	1.19	1.86	1.72
2A	973	1.22	1.73	7.88

the effect of palladium was to decrease the amount of ferrous ions remaining after reduction and produce a new chemical state of iron. The degree of removal of ferrous ions depended on both the temperature and the Pd loading. For reduction at 673°K, ferrous ions were no longer detectable in the spectrum at 4.75% Pd loading and the new iron species produced gave a quadrupole split spectrum with isomer shift $(\delta) = 0.28$ mm sec^{-1} and quadrupole splitting $(\Delta) = 0.46$ mm sec^{-1} based on the peak minima. For 973°K reduction, ferrous ions disappeared from the spectrum at 2.2% Pd loading and the Mossbauer spectrum showed a broad single peak with an $\delta = 0.33$ mm sec^{-1}. This same value was observed for Cat. D reduced at 973°K and is in excellent agreement with the value of 0.34 mm sec^{-1} reported for iron in bulk PdFe alloys (*12*) and with our previous studies on a 0.05% Fe, 2.2% Pd/η-Al_2O_3 sample (*9*). Figures 1E and 2E show spectra for a physically mixed catalyst with metal composition equivalent to Cat. D. The effect of palladium on iron reduction was greatly reduced in physical mixtures.

From this initial study, it was clear that palladium markedly alters the chemical nature of iron in PdFe/η-Al_2O_3. In addition, the similarity in behavior of the PdFe catalysts in this investigation to that reported previously (*9*) for PdFe/η-Al_2O_3 prepared in a different manner strongly indicates that bimetallic clusters of PdFe are formed. In the previous work, the analysis of the spectra were complicated by the presence of ferrous ions in all the spectra. However, as shown in Figs. 1D and 2D this complication is removed for Cat. D which gives "clean" spectra. More detailed studies of Cat. D were therefore undertaken in order to understand the nature of the iron in this material.

Oxidation–Reduction Behavior of Cat. D (0.1% Fe, 4.75% Pd/η-Al_2O_3)

The oxidation–reduction behavior of Cat. D was investigated in sequential experiments on the same sample. These results are shown in Fig. 3A–E and the Mössbauer parameters are summarized in Table 3. The Mössbauer parameters for Fig. 3A indicate that only ferric ions were present in the fresh material. The same result was also obtained for fresh Cat. A and was expected since ferric ion solution was used in the preparation of these materials. Evacuation and exposure of Cat. D to H_2 all at 298°K converted most of the iron to the ferrous state (Fig. 3B). The ferric ions in Cat. A, however, were unaffected by this treatment. In separate experiments on a fresh sample of Cat. D it was observed that reduction to the ferrous state also occurred on *exposure of the evacuated sample to CO at 298°K*. Cat. A, however, was unaffected by CO at 298°K. The Mössbauer parameters for the ferrous ions in Cat. D following CO reduction were $\delta = 1.16$ mm sec^{-1} and $\Delta = 2.19$ mm sec^{-1}. Palladium thus catalyzes the reduction of iron to the ferrous state on exposure of Cat. D *to H_2 or CO at 298*°K.

Reduction of Cat. D at 673°K gave Fig. 3C. As the first approximation, Fig. 3C was treated as two peaks and computer analysis gave the isomer shift and quadrupole splitting, based on the peak minima, shown in Table 3. The values in Table 3 are the averages of seven measurements covering four separate sample preparations. The asymmetry in the intensities of the peaks in Fig. 3C and their unequal linewidths suggest a distribution of chemical environments for the iron atoms giving a distribution of isomer shifts and quadrupole splittings. For a distribution of environments, the centroid of the spectrum is the proper measure of the average isomer shift rather than that determined from the peak minima. For Fig. 3C, the centroid shift was 0.34 mm sec^{-1}. For a distribution of environments, the areas of the two peaks should be equal. For Fig. 3C, however, the area of the high velocity peak was greater than that of the low velocity peak. This suggests that a Goldanskii–Karyagin effect

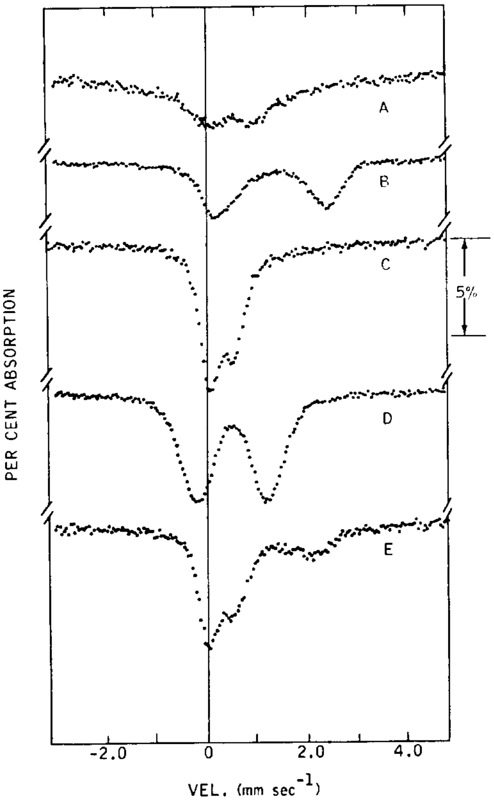

FIG. 3. Mössbauer spectra showing oxidation–reduction behavior of Catalyst D (0.1% Fe, 4.75% Pd/η-Al_2O_3). (A) As prepared in air; (B) evacuated, exposed to 1 atm H_2 at 298°K; (C) reduced in H_2, 1 hr at 673°K; (D) evacuated, exposed to 1 atm O_2 at 298°K; (E) evacuated, exposed to 1 atm H_2 at 298°K. All spectra recorded at 298°K.

in addition to the distribution of chemical states is important in Fig. 3C as discussed below. For a spectrum exhibiting both a multiplicity of chemical states and a Goldanskii–Karyagin effect, the centroid shift will be biased in the direction of the higher area peaks. The average isomer shift for Fig. 3C, therefore, lies within the range 0.28 mm sec^{-1} determined from the peak minima and 0.34 mm sec^{-1} determined from the centroid of the spectrum.

The chemical behavior of Cat. D reduced at 673°K [Cat. D [673]) in oxidation and reduction at 298°K is shown in Fig. 3D and E. Exposure of the reduced material to oxygen gives a nearly symmetric quadrupole doublet with broad lines (Fig. 3D). A two peak analysis of Fig. 3D gave parameters which are typical of high spin ferric ion and which are in good agreement with previous work on a 0.05% Fe, 2.2% Pd/η-Al_2O_3 catalyst (*9*). The χ^2/df for Fig. 3D could be significantly improved by the addition of more quadrupole doublets. A four-peak analysis lowered χ^2/df to 1.34 while a six-peak analysis gave a value of 0.93. Such results strongly suggest that spectrum Fig. 3D is due to ferric ions in a number of environments. In the absence of information of the number of iron environments present in Fig. 3D, we do not feel that it is meaningful to attach significance to computer analyses with more than two peaks. We accept the parameters from the two-peak analysis as an average value for the chemical states of iron in Fig. 3D. The important result is that the iron in Cat. D

TABLE 3

Mössbauer Parameters for Cat. D (0.1% Fe, 4.75% Pd/η-Al_2O_3) for Various Treatments

	1	2	3	4	Peaks	δ	Δ	χ^2/df
Fig. 3A, air at 298°K	−0.01	0.96	—	—	1–2	0.47	0.96	0.90
Fig. 3B, H_2 at 298°K	0.23	2.36	—	—	1–2	1.30	2.13	1.96
Fig. 3C, H_2 at 673°K, 1 hr	0.05 (±0.02)	0.51 (±0.01)	—	—	1–2	0.28 ± 0.01	0.46 ± 0.03[a]	1.22–2.89
Fig. 3C, evacuated and O_2 added at 298°K	−0.24	1.23	—	—	1–2	0.48	1.45	3.68
Fig. 3E, evacuated and H_2 added at 298°K	0.02	0.41	0.57	2.11	1–3	0.29	0.55	1.02[b]
					2–4	1.26	1.70	

[a] Errors are average deviations for seven runs covering four separate preparations.

[b] The dips and widths of peaks 2 and 4 were constrained to be equal.

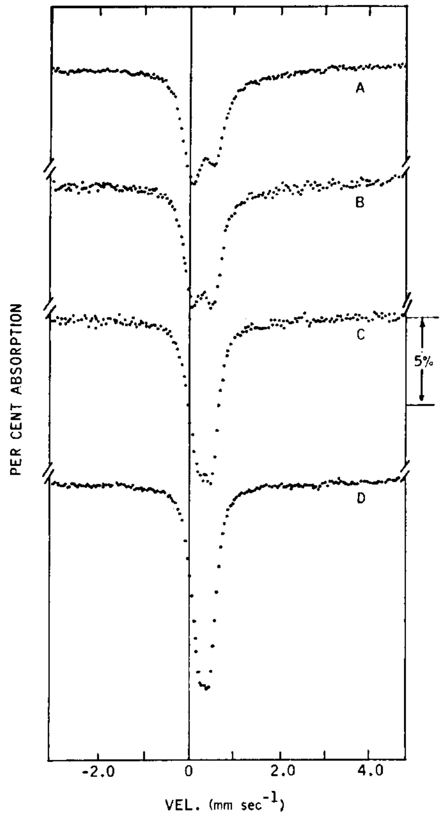

FIG. 4. Mössbauer spectra of Catalyst D (0.1% Fe, 4.75% Pd/η-Al_2O_3) reduced at various temperatures. Reduced in H_2 (A) 1 hr at 673°K; (B) 1 hr at 773°K; (C) 1 hr at 873°K, (D) 2 hr at 973°K. All spectra recorded at 298°K in 1 atm H_2.

(673) is oxidized to the ferric state on exposure to O_2 at 298°K.

Evacuation of the sample giving Fig. 3D followed by exposure to hydrogen all at 298°K gave Fig. 3E. Hydrogen at 298°K markedly altered the chemical state of the iron from the oxidized sample. The peak at ~2.1 mm sec^{-1} is the right half of a ferrous quadrupole doublet demonstrating that the iron in the oxidized sample can be reduced in H_2 at 298°K. Figure 3E was computer analyzed with four peaks with the constraints shown in Table 3. These constraints are reasonable since the left peak of the ferrous doublet would be expected to have nearly the same intensity and width as the right peak. Peaks 1–3 we assign to iron which is re-reduced to the metallic state and which is associated with palladium. The isomer shift for peaks 1–3 is identical to that obtained for Fig. 3C whereas the quadrupole splitting is larger by about 0.08 mm sec^{-1}. This difference in quadrupole splitting may be due to oxygen which is not removed by the titration as is indicated by the ferrous peaks in Fig. 3E. If we assume no difference in recoil-free fraction for iron species giving peaks 1–3 and 2–4, we estimate from the areas under the doublets that ~40% of the iron is incompletely reduced and is in the ferrous state in the sample giving Fig. 3E.

Agglomeration of Catalyst D

Further insight into the chemical nature of the iron in Cat. D was obtained from agglomeration studies. Palladium on alumina is readily agglomerated in hydrogen at elevated temperatures and thus the effect of agglomeration on the Mössbauer spectrum of the iron could be determined. Cat. D was reduced at successively higher temperatures from 673 to 973°K. Following reduction at each temperature a spectrum was recorded at room temperature in 1 atm of hydrogen and after evacuation and exposure to 1 atm of oxygen all at room temperature. On a separate sample the dispersion of Cat. D as a function of reduction temperature was determined following the hydrogen adsorption method of Aben (*11*).

The Mössbauer spectra for Cat. D for various reduction temperatures are shown in Fig. 4A–D. As a first approximation, the spectra in Fig. 4 were all computer analyzed assuming two peaks. The Mössbauer parameters for these analyses, the dispersions and calculated average particle sizes are tabulated in Table 4.

Increasing the reduction temperature from 673–973°K caused a fivefold decrease in dispersion. As the dispersion decreased the average quadrupole splitting of the spectra decreased indicating an increase in the average symmetry of the environment of the iron atoms. This trend is consistent with the presence of homogeneous PdFe clusters in which the surface to bulk ratio of iron atoms decreases with decreasing dispersion and a larger fraction of the iron "sees" a more symmetrical bulk-like environment. The behavior of Cat. D vs reduction temperature suggests that the Mössbauer spectra can be conveniently divided into surface (Fe_S) and bulk (Fe_B) iron atoms and that computer analysis for more than two peaks would be appropriate. This is especially true for the cases where dispersion measurements indicated that a substantial fraction of the iron atoms occupied surface sites. The spectra of Fig. 4 were thus computer analyzed for three peaks assuming a single line for Fe_B and for four peaks assuming a doublet for Fe_B. These analyses improved the "goodness of fit" for all spectra. For the three-peak analysis the isomer shift of the central peak varied from 0.10 to 0.39 mm sec^{-1}, while the isomer shift for peaks 1–3 varied from 0.22 to 0.30 mm sec^{-1} in no consistent manner. In addition the asymmetry and area of peaks 1–3 varied markedly and the areas showed no monotonic trend with decreasing dispersion as would be expected. Four-peak computer analysis gave similar results. Only the two-peak analysis gave results which were consistent for measurements on samples from separate preparations. The significant trend observed in the two-peak analysis is a collapse of the average quadrupole splitting with decreasing dispersion.

TABLE 4

Mössbauer Parameters and Dispersions for Cat. D Reduced at Various Temperatures

Reduction temp (°K)	δ (mm sec^{-1})	Δ (mm sec^{-1})	χ^2/df	H/M (1 mm Hg, 343°K)	Calcd particle size[a] (nm)
673	0.28	0.46	1.22	0.54	2.5
773	0.28	0.44	1.29	0.31	4.7
873	0.33	0.31	1.07	0.22	7.0
973	0.33	0.24	1.95	0.11	14.6

[a] Length of edge of fcc octahedron assuming adsorption on all eight faces.

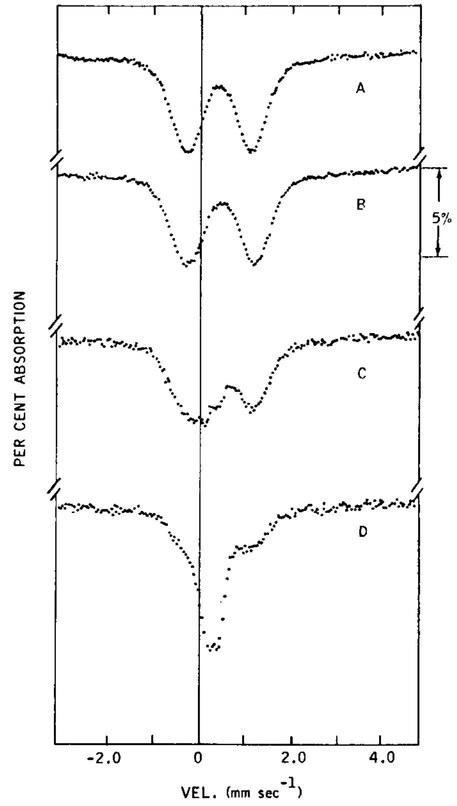

FIG. 5. Mössbauer spectra of Catalyst D (0.1% Fe, 4.75% Pd/η-Al_2O_3) reduced at various temperatures followed by evacuation and exposure to 1 atm O_2 at 298°K. Exposed to oxygen after reduction (A) 1 hr at 673°K; (B) 1 hr at 773°K; (C) 1 hr at 873°K; (D) 2 hr at 973°K. All spectra recorded at 298°K in 1 atm O_2.

The decrease in surface iron to bulk iron ratio on reducing Cat. D at successively higher temperatures is readily apparent after exposing the samples to O_2 at 298°K. This is shown in Fig. 5A–D. With increasing reduction temperature and decreasing dispersion the effect of oxygen on the spectrum of the reduced samples clearly changes. Peaks due to Fe^{3+} are discernible in all spectra but their intensity decreases with decreasing dispersion. For reduction at 673 or 773°K oxygen exposure appears to affect all the iron converting it to Fe^{3+}. The spectra of oxidized Cat. D following reduction at 873 or 973°K show peaks in addition to the ferric ions (Fig. 5C and D). Computer analysis of these spectra for four peaks gave

TABLE 5

Mössbauer Parameters for Cat. D Reduced at Various Temperatures and Exposed to Oxygen at 298°K

Reduction temp (°K)	Peaks 1–4 (mm sec^{-1})		Peaks 2–3 (mm sec^{-1})		χ^2/df
	δ	Δ	δ	Δ	
673	0.48	1.45	—	—	3.68
773	0.48	1.51	—	—	3.27
873	0.44	1.56	0.30	0.35	1.16
973	0.51	1.37	0.30	0.26	1.05

the results shown in Table 5. The outer doublet in each case gives parameters similar to those for Fe^{3+} in Figs. 5A and B. The parameters for the inner doublets are in good agreement with those obtained for Figs. 4C and D for the reduced samples (Table 4). This strongly supports the contention that the inner doublets in Figs. 5C and D are due to iron in the interior of the PdFe clusters. This iron is unaffected by oxidation of the surface of the clusters.

Comparison of Dispersion from Chemisorption and Mössbauer Measurements

Dispersions from hydrogen chemisorption measurements on Cat. D reduced at various temperatures are reported in Table 4. The Mössbauer spectra of the reduced samples could not be resolved with confidence into surface and bulk peaks precluding an evaluation of dispersion from these spectra. Room temperature oxidation of the reduced samples, however, showed both surface (as Fe^{3+}) and bulk peaks for samples reduced at 873 and 973°K (Fig. 5). Providing the areas under the respective peaks can be accurately determined and the relationship between the area for a given species and its concentration are known, the dispersion of Cat. D can be calculated from the spectra of the oxidized samples. Implicit in such a calculation are the assumptions that the particles are uniform in composition and that only the iron at the surface of the particles is affected by oxygen adsorption.

The normalized area under a well-resolved Mössbauer absorption line of Lorentzian shape is given by

$$A = \frac{\pi}{2} f_s f_a \sigma_0 \Gamma n G(t_a), \qquad (1)$$

where f_s and f_a are the recoil-free fractions for the source and absorber, respectively, σ_0 is the cross section for gamma ray adsorption at the resonant maximum, Γ is the experimental full width of the absorption line at half-maximum, n is the concentration of the Mössbauer isotope (atoms cm^{-2}), and $G(t_a)$ is the correction due to finite thickness of the absorber. The dimensionless absorber thickness is given by $t_a = \sigma_0 f_a n$. The function $G(t_a)$ has been presented in graphical form by Havens and Rainwater (*13*) and has the behavior $G(t_a) \to 1$ as $t_a \to 0$. Absolute area calculations, of course, require that the parameters in Eq. (1) be evaluated and that background radiation corrections be applied.

For a sample containing two chemical states of the Mössbauer isotope, the ratio of the number of atoms in the two chemical states may be obtained by the area ratio method (*14*).

$$A_1/A_2 = \frac{\Gamma_1 f_1 G[t_a(1)] n_1}{\Gamma_2 f_2 G[t_a(2)] n_2} = C \frac{n_1}{n_2}. \qquad (2)$$

This method reduces the number of parameters to be evaluated and eliminates errors due to background since this correction is the same for both species.

Equation (2) is strictly applicable only in the case of thin absorbers where the peaks for the two species are well resolved and of Lorentzian shapes. For Figs. 5C and D use of Eq. (2) is complicated by incomplete resolution of the Fe^{3+} peaks from the Fe in Pd peaks and by the presence of a distribution of iron environments. Recognizing these difficulties it is nevertheless instructive to compare the dispersion of Cat. D calculated from Mössbauer spectra with that determined by hydrogen chemisorption. Using Eq. (2) the dispersion of Cat. D from Figs. 5C and D becomes

$$D = \frac{100}{C(A_{\mathrm{FePd}}/A_{\mathrm{Fe}^{3+}}) + 1}. \qquad (3)$$

The respective areas for Fe^{3+} and FePd in Figs. 5C and D were determined by computer analysis with the constraints that the percentage effect and linewidths of the Fe^{3+} peaks be equal. This is justified by the analysis of Fig. 3D for Cat. D where the percentage effect and width for the two Fe^{3+} peaks are nearly identical. The central peaks in Figs. 5C and D were treated as quadrupole doublets with no constraints.

Table 6 summarizes the dispersions from chemisorption and Mössbauer spectra. With a value of $C = 1$ it is clear that the dispersions from spectral areas are much larger than the chemisorption values. Peaks due to FePd are not detectable in Figs. 5A and B and for Figs. 5C and D values of 15 and 8, respectively, are required for C to give reasonable agreement with chemisorption. These values are unrealistic as the following estimate demonstrates. For the Mössbauer sample used in Fig. 5, $t_a = nf_a\sigma_0 \approx 1$ assuming a reasonable value of $f_a \approx 0.6$. For $t_a \approx 1$, $G(t_a) \approx 0.8$. Figure 6C and D, however, are composed of more than one line and thus the t_a per line would be <1 and $G(t_a) > 0.8$. It seems reasonable therefore that $G(t_a)_{\mathrm{Fe}^{3+}}/G(t_a)_{\mathrm{FePd}} \approx 1$. For the ratio of the recoil-free fractions we use the method of Housley *et al.* (*10*). The relative area for a thin ($t_a \approx 0.3$) sample of Cat. D reduced at 673°K and exposed to O_2 at 298°K to that of the same sample reduced at 973°K gave the ratio $f_{\mathrm{Fe}^{3+}}/f_{\mathrm{FePd}} = 0.97 \approx 1$ and $\Gamma_{\mathrm{Fe}^{3+}}/\Gamma_{\mathrm{FePd}} \approx 2$. Thus we estimate a value for C of ~ 2. The lack of agreement between the dispersions determined from chemisorption and spectral areas therefore appears due to other effects than can be accounted for by C in Eq. (3). These are considered in the discussion.

TABLE 6

Comparison of the Dispersion of Cat. D from Hydrogen Chemisorption and Mössbauer Spectra

Reduction temp (°K)	D (H_2 chemisorption)	D from Mössbauer spectra ($C = 1$)
673	54	100
773	31	100
873	22	81
973	11	50

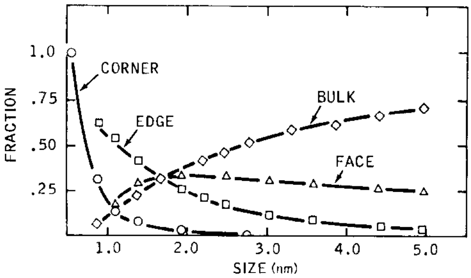

FIG. 6. Fraction of atoms occupying corner, edge, face and bulk sites in an fcc octahedron as a function of particle size.

DISCUSSION

In this section the implications of the chemical behavior of fresh Cat. D at room temperature are first discussed. Next the Mössbauer spectrum of Cat. D reduced at 673°K and the behavior of Cat. D in the reduced state and in the oxidized state as a function of dispersion are considered. Finally the chemical behavior of reduced Cat. D in oxidation and reduction at room temperature is discussed.

The chemical behavior observed for Cat. D in the present study was, in general, the same as that reported previously for a 0.05% Fe, 2.2% Pd/η-Al_2O_3 catalyst (*9*). In the previous work it was concluded that PdFe clusters were present in the reduced catalysts. The spectra, however, were complicated by the presence of ferrous ion peaks due to incomplete reduction of the iron. This made resolution of the spectra difficult and obscured details which were uncovered here. For Cat. D in this investigation complications due to ferrous ions were not present allowing the chemical changes and parameters for the iron to be more accurately determined. The present study thus extends and refines the previous work and provides firm evidence for PdFe bimetallic clusters in catalysts prepared by the usual impregnation, calcination and reduction procedures and employing a typical Al_2O_3 support.

Reduction of PdFe/η-Al_2O_3 at Room Temperature

The reduction of fresh Cat. D to the ferrous state on exposure to hydrogen at 298°K demonstrates the catalytic effect of palladium on iron reduction. We have argued (*9*) that this result is evidence for contact between the particles containing Pd and Fe and that Pd catalyzes the reduction of iron by hydrogen spillover across the interfacial contacts between the particles rather than by spillover involving migration of a hydrogen species over the Al_2O_3 support. The result in the present study that the iron in Cat. D was reduced to the ferrous state in CO at 298°K lends additional support to this model for a fresh catalyst. It is difficult to envision how CO could be activated on Pd, spillover onto Al_2O_3, diffuse to iron oxide particles and promote reduction. The results with CO, in fact, indicate that the contacts between Pd and Fe particles are not just of a physical nature but rather the Pd chemically alters the iron in such a way that the bond between oxygen and iron is sufficiently weakened to allow reduction by CO at 298°K. A similar argument applies to reduction in the presence of H_2.

The Mössbauer Spectrum of Dispersed PdFe Bimetallic Clusters

The isomer shift of 0.28–0.34 mm sec^{-1} observed for Cat. D (673) is close to the value of 0.34 mm sec^{-1} reported for dilute iron in bulk PdFe alloys (*12, 15*). Bartholomew and Boudart (*16*) found that the isomer shift for iron in PtFe clusters in PtFe/carbon catalysts was close to the value of 0.52 mm sec^{-1} observed for iron in PtFe alloys (*12*). We have also observed an isomer shift of ~0.5 mm sec^{-1} for well-dispersed PtFe clusters on η-Al_2O_3 (*17*). These results demonstrate that the iron in these catalysts is associated with the noble metal in each case and that the function of the noble metal is not simply one of catalyzing the formation of an iron species independent of the noble metal. The effect of absorbed hydrogen on the isomer shift of PdFe clusters has been discussed previously (*9*).

The quadrupole splitting observed for Cat. D (673) indicated that the iron atoms occupy sites of non-cubic symmetry. If all of the iron in Cat. D alloyed with all of the palladium, the average composition would be 3.8 atomic% iron. For a homogeneous bulk alloy of this composition with fcc structure the Pd/Fe ratio is 25 and each iron atom has only palladium nearest and next nearest neighbors. The Mössbauer spectrum at 298°K for a bulk alloy would be a single line with no resolved quadrupole splitting (*15*). The quadrupole splitting for Cat. D (673) is thus indicative of iron associated with palladium as well-dispersed clusters in which a large fraction of the iron is present at the surface of the clusters. This is confirmed by chemisorption measurements which showed Cat. D (673) to have 54% dispersion and by the fact that exposure of the reduced sample to oxygen at 298°K converted all the iron to the ferric state. The isomer shift and quadrupole splitting observed for Cat. D (673) are thus consistent with well-dispersed PdFe bimetallic clusters.

The unequal intensities and linewidths observed for Fig. 3C are attributed in part to a distribution of iron chemical states. It is easy to see from Fig. 6 how a distribution of environments may arise for small particles even considering an idealized case. For small particles $< \sim 5$ nm, the iron atoms at the surface may occupy sites with different symmetries and coordination numbers producing a distribution of isomer shifts and quadrupole splittings. A similar conclusion is reached when other crystallite models[1] are considered.

Other factors which contribute to broadening the distribution of possible iron environments are imperfections in the bimetallic clusters and perturbations on the atoms in the clusters due to contact between the cluster surface and the ions which make up the support. Contacts of the latter sort would certainly produce different electric field gradients at the points of contact than would be present at the gas–metal interface.

Other possible sources of the asymmetry observed for Cat. D (673) are the Goldanskii–Karyagin effect (*18*) and relaxation phenomena (*19*). The former results from anisotropy in the vibrations of the Mössbauer atoms and is to be expected for atoms at a surface. The latter results from the presence of fluctuating fields at the Mössbauer nucleus on the time scale of the Larmor precision frequency. For a thin absorber and a single chemical state of iron the Goldanskii–Karyagin effect gives a doublet with peaks of unequal intensities and areas but equal linewidths. Relaxation effects, however, give a doublet with peaks of unequal intensities and linewidths but equal areas. For Cat. D (673), all of these parameters are unequal for the peaks of the doublet. This is consistent with a combination of a distribution of chemical environments and a Goldanskii–Karyagin effect.

For the Goldanskii–Karyagin effect the asymmetry in the doublet increases with increasing temperature. With relaxation effects the temperature dependence of the asymmetry depends on the relaxation mechanism. For the Mössbauer effect the important mechanisms are electronic spin–lattice and spin–spin relaxation. With ^{57}Fe in alloys spin–lattice relaxation is the fastest process due to the strong interaction between the conduction electrons and the *d*-electrons which are responsible for the localized magnetic moment (*20*). In the case where spin–lattice relaxation is fast compared to the other processes, the asymmetry in the Mössbauer doublet decreases with increasing temperature. For Cat. D (673) temperature dependence studies over the range 83–626°K showed an increase in the area asymmetry with increasing temperature indicative of a Goldanskii–Karyagin effect, which is to be expected for small particles where surface effects predominate. The asymmetry in the spectrum of Cat. D (673), therefore, most likely results from a combination of distribution of chemical environments and a Goldanskii–Karyagin effect.

Agglomeration of PdFe/η-Al_2O_3

The collapse of the quadrupole splitting accompanying the increase in reduction temperature for Cat. D and the decrease in the amount of iron which could be oxidized at 298°K are additional evidence for PdFe bimetallic clusters. Dispersion measurements showed a decrease in the surface to volume ratio with increasing reduction temperature consistent with the trend in the Mössbauer spectra. As dispersion decreases more of the iron assumes a symmetric bulk environment producing a collapse of the quadrupole splitting. The increase in the isomer shift for the lowest dispersion to 0.33 mm sec^{-1}, a value in good agreement with that for dilute iron in bulk PdFe alloys, provides further support for this model.

For all reduction temperatures between 673 and 973°K the Mössbauer spectra of reduced Cat. D could not be resolved with confidence into surface and bulk peaks. For Cat. D (673) with 54% dispersion this is not unreasonable since inspection of a model of a homogeneous octahedral PdFe cluster with this dispersion shows that 83% of the atoms are contained in the first two

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[1] A summary of the fraction of atoms occupying various sites for different crystalline shapes as a function of size is given by Anderson (*28*, p. 244).

surface layers. Atoms on or in the surface layer should exhibit a resolved quadrupole splitting due to the asymmetry at the surface (*21*). In addition, atoms in the subsurface layers may experience sizable electric field gradients as a result of bonding to the coordinately unsaturated surface atoms whose chemical state in vacuum or when bonded to absorbates may differ from that of the atoms in the underlying layers. That this is the case for palladium particles is suggested by the results of Benson *et al.* (*22*) in which it was shown that evacuation of hydrogen saturated palladium catalysts for short times at room temperature destroyed the bulk β-phase hydride but did not remove hydrogen from the surface palladium atoms. This demonstrates that the surface Pd–H bond is much different than the bulk Pd–H bond. Other factors which can produce field gradients in the subsurface layers are imperfections due to missing atoms at the surface and field gradients produced by the ions of the support in contact with the clusters.

With increasing particle size surface and bulk peaks should become distinguishable if they are sufficiently resolved from each other. Unfortunately for Cat. D in this investigation the surface and bulk peaks in the *reduced* samples always overlapped in such a manner that we could not, even with computer analysis, resolve them with any certainty. The use of a source with a smaller linewidth than that used here may be more advantageous for resolving surface and bulk peaks.

The presence of both surface and bulk iron in Cat. D was conclusively demonstrated by exposing the samples reduced at 873 and 973°K to oxygen at room temperature. In both cases "surface" iron as Fe^{3+} and "bulk" iron which is not converted to Fe^{3+} on oxidation were distinguishable in the Mössbauer spectra. The dispersions of Cat. D determined by hydrogen chemisorption for various reduction temperatures did not agree, however, with the values estimated from the spectra of the samples exposed to oxygen at 298°K. The dispersions from the latter were always much larger than those from hydrogen chemisorption. Several possible sources for this discrepancy must be considered. These include differences in the dispersions of samples used in Mössbauer and chemisorption experiments, surface segregation of the iron, concentration of iron in the smallest palladium particles and local heating effects.

The Mössbauer spectra of Cat. D and the dispersion measurements were run on separate samples of the same material which were treated with the same hydrogen source using identical procedures. We do not believe that the differences in geometry[2] with respect to hydrogen flow would give larger dispersions in the Mössbauer experiments than in the dispersion measurements. Based on current theories of surface enrichment in binary alloys, it is expected that the component with the lower heat of sublimation will segregate to the surface (*5*). For iron and palladium the heats of sublimation are comparable and surface segregation of iron is not expected. Even in cases where surface segregation is favored for the bulk alloy, the surface composition approaches the bulk composition with increasing dispersion (*23*). Differences in the dispersions of the samples used in the Mössbauer and chemisorption experiments or surface segregation do not appear to account for the discrepancy between dispersions determined from chemisorption and Mössbauer spectra.

In this work the catalysts were prepared by first depositing the palladium on the η-Al_2O_3 followed by drying and calcination and then depositing the iron. A distribu-

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[2] For the dispersion measurements, hydrogen flowing at 500 ml/min was passed through 20–40 mesh catalyst particles in the downflow configuration. For the Mössbauer experiments, the hydrogen flow was also 500 ml/min but did not impinge directly on the catalyst wafer. The wafer was held in the center of a heated tube 2.2 cm in diameter and 5.1 cm in length and hydrogen flowed passed the ends of the tube.

tion of particle sizes undoubtedly existed in the Pd/η-Al_2O_3 prior to iron addition.[3] It is reasonable to expect that the probability of contacts between iron containing and palladium containing particles will increase, at a given iron loading, as the palladium loading is increased at constant dispersion. The results in Fig. 1, in fact, support such a model. Furthermore, for a given iron and palladium loading, the probability of contacts should increase the higher the dispersion of the palladium. We have, in fact, observed this to be the case for several supported iron–Group VIII bimetallic catalysts. From these considerations it is reasonable to expect that the iron in PdFe/η-Al_2O_3 catalysts is associated to a greater extent with the palladium crystallites of higher dispersion. This model can account for the larger dispersions of Cat. D determined from Mössbauer spectra compared to the dispersions from hydrogen chemisorption.

Another possible source of the discrepancy between dispersion from Mössbauer spectra and hydrogen chemisorption is oxidation of iron below the surface layer. The calculation of dispersions from Mössbauer spectra was based on the assumption that only the surface iron atoms are oxidized. This appears to be a poor assumption based on other studies reported in the literature. Ratnasamy *et al.* (*24*), using the radial electron distribution technique, concluded that oxygen adsorption on alumina-supported Pt clusters caused complete disordering of the first *two* surface layers. Williams and Boudart (*25*), using Auger electron spectroscopy, showed that oxygen chemisorption on NiAu foils enriched the surface in nickel due to the much stronger bond between nickel and oxygen compared to gold and oxygen. The large heat of adsorption of oxygen on iron (136 kcal/mole) compared to palladium (67 kcal/mole) could produce a similar result in PdFe clusters. The large exothermic heat of oxygen adsorption and the heat from reaction of oxygen with residual hydrogen absorbed in or adsorbed on the PdFe clusters can produce local temperature excursions (*26*) which facilitate disruption of the surface layers as proposed by Ratnasamy *et al.* and the diffusion of iron atoms from the subsurface layers to the surface. Thus concentration of the iron in the more highly dispersed Pd particles and oxidation of iron below the surface layers appear to be the most reasonable explanations for the discrepancy between dispersion from Mössbauer spectra and chemisorption.

Chemical Behavior of PdFe/η-Al_2O_3

The iron in reduced Cat. D which could be oxidized to Fe^{3+} in oxygen could also be reduced in hydrogen at 298°K. This behavior is identical to that observed by Bartholomew and Boudart (*16*) for PtFe clusters on carbon. The reversible oxidation–reduction of the iron in those catalysts is convincing evidence that bimetallic clusters are formed since unalloyed iron particles would not reduce in hydrogen at 298°K.

Figure 3E shows that the reduction of oxidized Cat. D (673) at 298°K in hydrogen is not complete. This is indicated by the presence of ferrous ions in the spectrum. The reduction, however, was more complete than when fresh Cat. D was exposed to hydrogen at 298°K (Fig. 3B). In the latter case, the sample was calcined in air at 773°K before exposure to hydrogen at room temperature. The metals were undoubtedly present as the oxides in this case with some form of contact between the oxides as discussed above. The lack of intimate homogeneous mixing of these oxides, however, may make reduction less complete than for oxidized Cat. D (673). In the latter the reduction at 673°K would promote homogeneity of the individual bimetallic clusters. Exposure of these clusters to oxygen forms a layer of oxide which is readily titrated by hydrogen at 298°K.

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[3] Many examples of broad particle size distributions in this type of catalyst are given by Anderson (*28*, p. 163).

With the high Pd/Fe ratio in Cat. D the iron atoms should have only Pd nearest neighbors and this apparently weakens the iron–oxygen bond to allow reduction at 298°K. The fact that some of the iron in oxidized Cat. D (673) can only be reduced to the ferrous state at 298°K indicates that all of the iron atoms are not equivalent. This could be explained by the formation of some PdFe clusters with lower Pd/Fe ratios than calculated from the nominal catalyst composition. The concentration of the iron in the more highly dispersed clusters, as discussed above, may account for this. Iron in these clusters may have iron near-neighbors which make the removal of oxygen more difficult as suggested by Bartholomew and Boudart (*16*) for PtFe clusters on carbon.

SUMMARY AND CONCLUSIONS

In this investigation direct evidence for bimetallic clusters as proposed by Sinfelt has been obtained for PdFe/η-Al_2O_3 catalysts prepared by the usual techniques of impregnation, drying and calcination in air. The general features of the Mössbauer spectra and chemical changes with treatment which provide evidence that bimetallic PdFe clusters are formed in the reduced catalysts are the following. In the absence of palladium, ferric ions on Al_2O_3 in low concentrations are unaffected by H_2 or CO at 298°K and can only be reduced to the ferrous state in H_2 at 973°K. In the presence of palladium the iron is reduced to the ferrous state at 298°K in H_2 or CO and reduction in H_2 at 673°K gives a quadrupole split spectrum with isomer shift close to that expected for dilute iron in bulk PdFe alloys. The iron in this material can be reversibly oxidized in oxygen and reduced in hydrogen at 298°K. The reversible oxidation–reduction of the iron in these catalysts is convincing evidence for bimetallic clusters since small iron particles covered with an oxide layer would not reduce in hydrogen at 298°K. The reversible oxidation–reduction behavior is the same as that observed by Bartholomew and Boudart (*16*) for PtFe/carbon catalysts. The isomer shift for iron in reduced PtFe/carbon catalysts was nearly identical to that observed for iron in bulk PtFe alloys while the isomer shift for Cat. D was close to that reported for bulk PdFe alloys demonstrating that the iron is associated with the noble metal in each case.

Increasing the reduction temperature of PdFe/η-Al_2O_3 caused a collapse of the quadrupole splitting observed in the 673°K reduced sample to a broad single line in the 973°K reduced sample. At the same time the amount of iron in the catalyst which could be converted to the ferric state on exposing the samples to oxygen at 298°K decreased and peaks due to unoxidized iron in the interior of the palladium as well as ferric ion peaks due to "surface" iron were discernible in the Mössbauer spectra. Chemisorption measurements showed a fivefold decrease in dispersion of the PdFe/η-Al_2O_3 on increasing the reduction temperature from 673 to 973°K. These observations are all consistent with expected changes in surface/volume ratio on agglomerating metal particles and provide a convincing case for bimetallic clusters.

Attempts to determine the dispersions of PdFe/η-Al_2O_3 catalysts from Mössbauer spectra of the reduced or reduced and oxidized samples were not successful. In reduced samples the surface and bulk iron peaks could not be resolved with sufficient confidence to allow the dispersion to be evaluated. For reduced catalysts exposed to oxygen at room temperature "surface" iron as Fe^{3+} and "bulk" iron as FePd could be resolved in some cases. Dispersions determined from such spectra were much larger than those determined by hydrogen chemisorption. This discrepancy was attributed to concentration of the iron in the smallest palladium particles and to oxidation of iron from the surface *and* subsurface layers on exposing the reduced catalyst to oxygen.

From this investigation it is apparent that the Mössbauer technique is capable of providing important insight into the chemical nature of supported metal catalysts. For properly chosen systems a number of important questions such as the effect of particle size on chemical state, the effect of promoters, metal–support interactions and factors affecting multimetallic cluster formation in supported catalysts should be amenable to investigation. Because of the distribution of chemical environments inherent to any supported metal catalysts, the technique probably cannot provide details of the microstructure of supported clusters. The combination of techniques such as EXAFS (*27*) which do give information on the microstructure with the Mössbauer effect on the same catalysts should give much insight into chemical nature and structural features of supported bimetallic catalysts.

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