JOURNAL OF CATALYSIS 35, 232–246 (1974)

The Chemical State of Iron in Reduced $PdFe/Al_2O_3$ Catalysts

R. L. GARTEN*

Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

AND

D. F. OLLIS

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540

Received March 18, 1974

Mössbauer spectroscopic studies show that ferric ions in low concentrations (0.05 wt%) on η-Al_2O_3 are unaffected by hydrogen at room temperature and can only be reduced to the ferrous state at temperatures as high as 700°C. Ferric ions in $PdFe/\eta$-Al_2O_3 catalysts, however, are reduced to the ferrous state at room temperature and to the metallic state at 500°C with formation of PdFe alloys. The results of this investigation are consistent with a model in which the reduction of iron to the metallic state and formation of PdFe alloys requires contact between a palladium particle and the oxide of iron which is reduced. Hydrogen "spillover" does occur but only across the interfacial contacts between palladium particles and the iron oxide. No evidence was found to support a model, proposed by others, in which ferromagnetic iron metal is formed in reduced $PdFe/Al_2O_3$ catalysts as a result of the diffusion of hydrogen over the support surface from palladium particles to an oxide of iron.

INTRODUCTION

In recent years several investigations have been reported which demonstrate that the hydrogen reduction of *supported* metal oxides, such as those of nickel and iron, is catalyzed by platinum-group metals. Roman and Delmon (*1*) observed that at 325°C the rate and extent of reduction of nickel oxide supported on silica were increased by the addition of palladium or platinum to the catalyst. Novak and Koros (*2*) and Novak (*3*) have shown that the incorporation of small amounts of palladium or platinum into alumina-supported nickel catalysts enhances synergetically the activity of the reduced catalysts for the hydrogenolysis of heptane. Sancier and Inami (*4*) found that small amounts of iron in supported platinum and palladium catalysts produced an intense electron spin resonance signal with a *g* value of 2.10 when the catalysts were reduced at 500°C. This signal was not observed for samples reduced at 500°C in which platinum or palladium were absent.

There are primarily two models which have been proposed to explain the catalyzed reduction of supported iron and nickel oxides. In the first model the role of the catalytic metal is not only to activate (dissociate) hydrogen but also to provide sites for the nucleation and growth of the metal phase formed by reduction of the oxide (*1, 2*). This model requires actual contact between the oxide to be re-

---

* To whom queries concerning this paper should be sent: P.O. Box 45, Linden, NJ 07036.

duced and the catalytic metal and hydrogen migration occurs only across the interfacial contacts.

In the second model the function of the catalytic metal is to activate hydrogen which subsequently diffuses over the support to the metal oxide and reduces it to the metallic state (*3, 4*). In this model the catalytic metal need not be in contact with the oxide and hydrogen migration is postulated to take place over distances large compared to the diameters of the catalytic metal or oxide particles. Sancier and Inami (*4*) proposed, for example, that ferromagnetic iron domains were produced in the presence of platinum or palladium by the following series of steps:

1. Activation (dissociation) of hydrogen on platinum or palladium.
2. Migration of hydrogen atoms over the support to iron oxide particles where reduction to metallic iron occurred.
3. Agglomeration of the metallic iron into crystallites large enough to exhibit ferromagnetism.

The large ESR spin intensities and the g value of 2.10 which agrees with that reported for dispersed iron (*5*) were taken as evidence for the presence of ferromagnetic iron in the reduced catalysts. Furthermore, Sancier and Inami concluded that the formation of ferromagnetic iron metal was evidence that hydrogen migrates across the surface of the support during reduction.

The high sensitivity of ESR coupled with the large spin intensities expected for ferromagnetic metals would appear to make this technique attractive as a local probe for hydrogen migration in supported catalysts as pointed out by Sancier and Inami. The identification of the chemical species giving rise to such ESR signals is not unambiguous, however. The observations of Sancier and Inami may be interpreted as evidence for alloy formation between iron and palladium rather than as evidence for hydrogen migration. Indeed, bulk palladium–iron alloys also give rise to an ESR signal with a g value of $\sim$2.10 (*6*). In addition, the high sensitivity of the ESR technique may detect chemical species which are present only in minor concentrations in the catalyst and lead to an incomplete picture of the chemical nature of the supported metals. In view of these considerations further study of the reduction of supported iron in the presence of platinum group metals seemed warranted.

In this investigation we have used Mössbauer spectroscopy to probe the chemical states of iron in ^{57}Fe-doped palladium on alumina catalysts. The Mössbauer technique has the advantage of being sensitive to small concentrations of ^{57}Fe and provides direct information on the chemical states of all of the iron atoms in catalytic materials (*7*).

EXPERIMENTAL METHODS

Materials

The support material used in this investigation was η-Al_2O_3 prepared by calcining Davison β-trihydrate of alumina for 4 hr in air at 590°C. The surface area of the final preparation was 245 $m^2\ g^{-1}$. The supported metal catalysts were prepared by impregnating the alumina with metal solutions of the proper concentrations in a ratio of 0.5 ml of metal solution/g of η-Al_2O_3. The impregnating solution was added to the support a few drops at a time with thorough mixing between additions. The palladium solution was prepared by dissolving palladium black (obtained from Engelhard Industries, Inc.) in aqua regia. Ferric oxide, 93% isotopically enriched in ^{57}Fe, was obtained from Oak Ridge National Laboratories. The enriched Fe_2O_3 was reduced in hydrogen for 2 hr at 450°C and then dissolved in 6 N HNO_3. The resulting solution was evaporated to near dryness twice with redilution in distilled water after each evaporation. The final solution has a pH $\approx$ 1.

The catalysts used in this investigation are described below:

Catalyst A: 0.05 wt% Fe/η-Al_2O_3. A sample of η-Al_2O_3 was reduced in hydrogen flowing at 200 cc min^{-1} for 4 hr at 400°C and 4 hr at 700°C. The sample was then impregnated with ^{57}Fe solution followed by drying in vacuum for 2 hr at 130°C.

Catalyst B: 2.2 wt% Pd/η-Al_2O_3. Palladium was impregnated onto η-Al_2O_3 followed by drying in air for 2 hr at 120°C. After drying the sample was reduced in hydrogen flowing at 200 cc min^{-1} for 4 hr at 400°C and 4 hr at 700°C.

Catalyst C: 0.05 wt% Fe, 2.2 wt% Pd/η-Al_2O_3. Catalyst B was impregnated with ^{57}Fe solution followed by drying in vacuum for 2 hr at 130°C.

Catalyst D: Physical mixture, 0.05 wt% Fe/η-Al_2O_3 + 2.37 wt% Pd/η-Al_2O_3. A sample of 0.1 wt% Fe/η-Al_2O_3 was prepared in the same manner as Catalyst A and physically mixed with an equal portion of a 4.75 wt% Pd/η-Al_2O_3 prepared in the same manner as Catalyst B. The physical mixing was carried out for 5 min in a Wig-L-Bug in which the powders were shaken vigorously in a closed thimble containing a stainless steel ball.

The preparative procedures described above were designed to follow closely those of Sancier and Inami and to ensure that the blank (Catalyst A) received the same pretreatment as Catalyst C.

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

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 thin wafers ⅞ in. in diameter. The Mössbauer cell was constructed from 304 stainless steel and had 10 mil beryllium windows. The gamma ray beam was collimated so that it passed only through the catalyst sample and the beryllium windows. The beryllium windows did not contain any detectable iron impurities as determined by blank experiments on the cell with no catalyst sample in place. The samples were heated by an external heater and the temperature was measured by a thermocouple located near the absorber wafer.

The Mössbauer spectra were recorded on an Austin Science Associated Mössbauer spectrometer using a ^{57}Co–Cr source. All isomer shifts are reported with respect to that source. A thin sodium nitroprusside absorber containing 8.7×10^{17} ^{57}Fe cm^{-2} gave a linewidth of 0.27 mm sec^{-1} when determined with the ^{57}Co–Cr source. The source was driven with constant acceleration and was slaved to an asymmetric wave form (Flyback mode) so that a single spectrum was recorded in the memory of an ND 2200 multichannel analyzer. Velocity calibration was obtained for every second channel of the multichannel analyzer by interferometry (*8*).

The Mössbauer spectra were computer analyzed by a variable metric minimization program which fits the data to Lorentzian line shapes and can be used with and without linear constraints. This program also computes the goodness of fit parameter (*9*)

$$\chi^2 = \sum_i \frac{(f_i^o - f_i)^2}{f_i}, \qquad (1)$$

where f_i^o are the observed counts in channel i and f_i are the calculated counts in channel i from the computer analysis. The statistical significance of the computer fit can be determined from standard tables (*10*) of χ^2/df where df is the number of degrees of freedom given by the number of data points used in the computer analysis less the number of adjustable parameters. Values of χ^2/df of <1.23 represent fits significant to the 1% level, i.e., if the experiment is repeated there is a 1% probability of obtaining a value of χ^2/df as large as 1.23.

The dispersion of the palladium catalysts was determined by hydrogen chemisorption on a volumetric adsorption apparatus following the method of Aben (*11*). With this method the hydrogen monolayer coverage of palladium is determined at 1 Torr hydrogen pressure (1 Torr = 133.3 N m^{-2}) and at 70°C. Under these conditions hydrogen absorption by the palladium is only 0.002 hydrogen atoms/palladium. Prior to the dispersion measurement Catalyst C was evacuated for 1 hr at 500°C, reduced 4 hr at 500°C and evacuated 2 hr at 400°C. Increasing the evacuation time had no effect on the hydrogen uptake. The reduction procedure duplicated the pretreatment conditions in the Mössbauer experiments. A reduction period of 4 hr was chosen since, as shown in Fig. 1 of the paper by Sancier and Inami (*4*), very little additional increase in the ESR spin density for PdFe/Al_2O_3 was observed for longer reduction times. In a separate experiment Catalyst C was reduced 2 hr at 700°C followed by a 1 hr evacuation at 500°C and then the dispersion was determined by Aben's method.

RESULTS

In order to understand the influence of palladium in palladium–iron catalysts it was first necessary to characterize the behavior of iron alone on η-Al_2O_3. To avoid ambiguities in interpreting the data, Catalysts A and D were prepared and pretreated in the same manner as Catalyst C. The changes in the chemical state of the iron in Catalysts A, C, and D were then followed by Mössbauer spectroscopy. For all catalysts spectra were obtained at room temperature (25 ± 2°C) in sequential experiments on the same sample and in 1 atm of the gas used in a particular treatment of the catalyst.

Catalyst A (0.05 wt% Fe/η-Al_2O_3)

The Mössbauer spectra obtained for various treatments of Catalyst A are shown in Fig. 1 and the Mössbauer parameters are summarized in Table 1. The catalyst as initially prepared gave a spectrum (Fig. 1a) typical of high spin ferric ions with an isomer shift (IS) of 0.48 ± 0.02 mm sec^{-1} and a quadrupole splitting (QS) of 0.94 ± 0.04 mm sec^{-1}. (Errors are standard deviations determined from the computer analysis). The presence of the ferric ions was to be expected since the iron was added to the support in the ferric state. Evacuation of Catalyst A followed by exposure to hydrogen all at room temperature did not alter the IS of the ferric ions and only slightly increased the QS to 1.02 ± 0.02 mm sec^{-1} (Fig. 1b).

Evacuation of Catalyst A for 1 hr at 500°C followed by hydrogen reduction for 4 hr at the same temperature gave Catalyst A-500 and converted the iron to the ferrous state as shown in Fig. 1c. The large linewidths of the peaks and asymmetric shape of the right peak in Fig. 1c suggests that more than one ferrous quadrupole doublet is present in the reduced sample. Computer analysis of spectrum 1c with four peaks gave an excellent fit to the data as did four peaks with certain linear constraints. As summarized in Table 1, the Mössbauer parameters for the two ferrous doublets depend on which combinations of peaks are assigned to the doublets. Peaks 1 and 2 at the lower velocities and peaks 3 and 4 at higher velocities can be combined in two ways (1–4 and 2–3 or 1–3 and 2–4) to give two ferrous doublets. Both of these combinations give Mössbauer parameters typical of high spin ferrous ions as shown in Table 1.

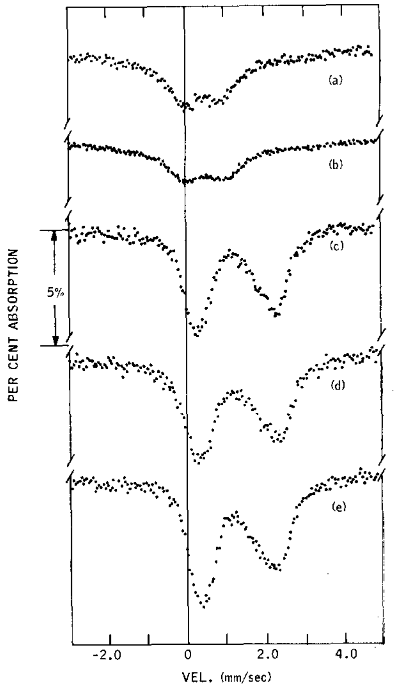

FIG. 1. Mössbauer spectra of Catalyst A (0.05 wt% Fe/η-Al_2O_3). (a) Catalyst as initially prepared; (b) exposed to H_2, 25°C; (c) evacuated 1 hr, 500°C, reduced in H_2, 4 hr, 500°C; (d) exposed to O_2, 25°C; (e) reduced 2 hr, H_2, 700°C.

TABLE 1

Summary of Mössbauer Parameters for Catalyst A (0.05 wt% Fe/η-Al_2O_3)

Fig.	No. of constraints		Peak combinations					
			1–4	2–3	χ^2/df	1–3	2–4	χ^2/df
1c	0	IS[a]	1.28	1.19	0.91	1.03	1.44	0.91
		QS	2.15	1.34		1.65	1.84	
	4	IS	1.29	1.27	1.00[b]	0.98	1.37	1.03[c]
		QS	2.12	1.32		1.66	1.95	
1d	4	IS	1.29	1.15	0.99[b]	0.99	1.38	0.99[c]
		QS	2.15	1.36		1.68	1.97	
1e	4	IS	1.30	1.14	1.24[b]	1.00	1.38	1.25[c]
		QS	2.05	1.28		1.52	1.88	

[a] IS and QS (mm sec^{-1}).

[b] The intensities and line widths of peaks 1 and 2 were constrained to be equal to those of peaks 4 and 3, respectively.

[c] The intensities and line widths of peaks 1 and 2 were constrained to be equal to those of peaks 3 and 4, respectively.

The introduction of linear constraints into a four-peak analysis of spectrum 1c did not significantly change the Mössbauer parameters compared to the unconstrained analyses. Constraints were applied in two ways. In the first case the intensities and line widths of the respective peak combinations 1–4 and 2–3 were constrained to be equal. In the second case these same constraints were applied to the peak combinations 1–3 and 2–4. Throughout this paper we shall refer to a ferrous doublet with the above constraints as a constrained ferrous doublet. As shown in Table 1 the goodness of fit parameter (χ^2/df) was not significantly increased by the introduction of constraints and the Mössbauer parameters for the ferrous doublets were essentially the same as those obtained in the unconstrained analysis regardless of the peak combinations chosen. Since there was little difference between the constrained and unconstrained analyses of the ferrous ion spectrum constrained analyses were used in subsequent data to analyze spectral peaks due to ferrous ions. The use of constraints in analyzing the ferrous portion of spectra proved useful in the analysis of the more complicated Mössbauer spectra from Catalyst C.

The ferrous ions formed in Catalyst A-500 were not reoxidized when the sample giving spectrum 1c was evacuated and exposed to oxygen all at room temperature (Fig. 1d). Table 1 shows that the Mössbauer parameters for spectrum 1d are practically the same as those determined for spectrum 1c of the reduced sample.

A more severe reduction of Catalyst A for 2 hr at 700°C [Catalyst A-700] had no effect on the IS of the ferrous ions but caused small decreases in the QS of both ferrous species (Fig. 1e and Table 1). No changes in the X-ray diffraction pattern of the η-Al_2O_3 were observed after the 700°C reduction when compared to the fresh material. As was previously observed for Catalyst A-500 no changes occurred in the spectrum of Catalyst A-700 on exposure to oxygen at room temperature.

Catalyst C (0.05 wt% Fe, 2.2 wt% Pd/η-Al_2O_3)

The Mössbauer spectra of Catalyst C showed markedly different behavior from that observed with Catalyst A. This is shown in Figs. 2 and 3 and in Table 2. Reduction of Catalyst C for 2 hr at 700°C [Catalyst C-700] gave Fig. 2a which shows only a small peak at ~2.5 mm sec^{-1} due to the right half of a ferrous doublet. The large peak at lower velocities shows clearly that a new iron species, not present in reduced Catalyst A, was formed on reduction of Catalyst C at 700°C. There was no evidence for ferromagnetic iron metal in

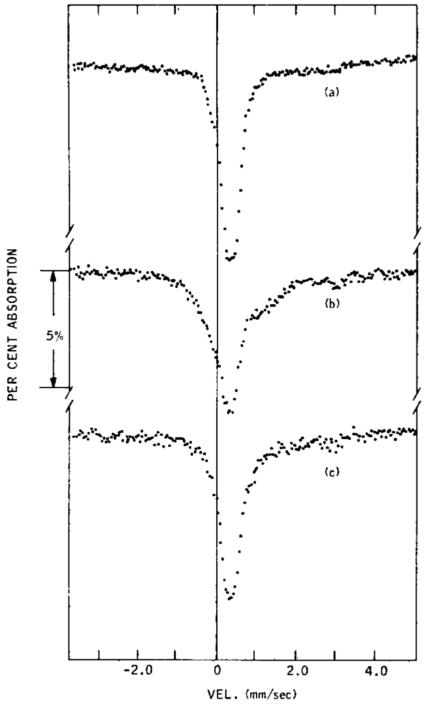

FIG. 2. Mössbauer spectra of Catalyst C (0.05 wt% Fe, 2.2 wt% Pd/η-Al_2O_3). (a) Reduced H_2, 2 hr, 700°C; (b) exposed to O_2, 25°C; (c) exposed to H_2, 25°C.

spectrum of the reduced sample. Spectrum 2a was computer analyzed for three peaks, i.e., a single peak and a constrained ferrous doublet. In the absence of constraints on the ferrous doublet an unreasonably large intensity for the left peak of the doublet was obtained. As shown in Table 2, the IS of the new iron species formed in Catalyst C-700 is 0.34 ± 0.02 mm sec^{-1}.

The chemical nature of the iron species formed in Catalyst C-700 was further investigated by evacuating the sample and exposing it to oxygen at room temperature. As shown in Fig. 2b new peaks appeared on either side of the large peak near ~0.3 mm sec^{-1}. Spectrum 2b was computer analyzed for 5 peaks assuming one constrained ferrous doublet. This analysis gave peaks at −0.22, 0.32 and 1.26 mm sec^{-1} in addition to a ferrous doublet (Table 2). The peak at 0.32 mm sec^{-1} is the same as the main peak in spectrum 2a. It does not seem reasonable that the peaks at −0.22 and 1.26 mm sec^{-1} are due to two chemical states of iron since this requires an assignment of the peak at −0.22 mm sec^{-1} to low spin Fe(II) or Fe(III) or to iron in an unusually high oxidation state of +4 (*12*). None of these assignments appears very probable in the present case. We feel more confident in assigning the peaks at −0.22 and 1.26 mm sec^{-1} to a quadrupole doublet with the parameters shown in Table 2. For this assignment the IS is typical of that expected for high spin ferric ion.

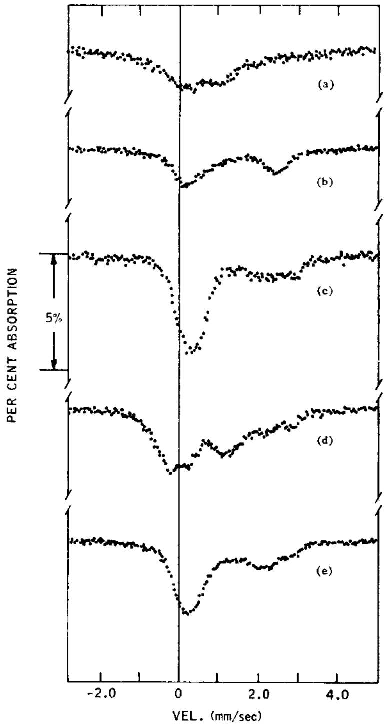

FIG. 3. Mössbauer spectra of Catalyst C (0.05 wt% Fe, 2.2 wt% Pd/η-Al_2O_3). (a) Catalyst as initially prepared; (b) exposed to H_2, 25°C; (c) evacuated 1 hr, 500°C, reduced H_2, 4 hr, 500°C; (d) exposed to O_2, 25°C; (e) exposed to H_2, 25°C.

When the sample giving spectrum 2b was evacuated at room temperature no changes occurred in the spectrum. Exposure of the evacuated sample to hydrogen at room temperature, however, removed the ferric species (Fig. 2c) and gave a spectrum similar to Fig. 2a. *Thus a portion of the iron in Catalyst C-700 could be reversibly oxidized in oxygen and reduced in hydrogen at room temperature.*

The behavior of Catalyst C at lower

TABLE 2

SUMMARY OF MÖSSBAUER PARAMETERS FOR CATALYST C (0.05 wt% Fe, 2.2 wt% Pd/η-Al_2O_3)

Fig.	No. of constraints	Peak positions (mm sec^{-1}) 1	2	3	4	5	6	Peaks	IS[a]	QS[a]	χ^2/df
2a	Intensity, width							2	0.34	—	
	peak (1) = peak (3)	0.10	0.34	2.81	—	—	—	1–3	1.46	2.71	1.66
2b	Intensity, width						—	3	0.32	—	
	Peak (2) = peak (5)	−0.22	0.05	0.32	1.26	3.00	—	1–4	0.52	1.49	0.90
								2–5	1.48	3.06	
3c	Intensity, width							2	0.29	—	
	peak (1) = peak (4)	−0.01	0.29	0.56	2.16	2.88	—	1–4	1.08	2.17	1.63
	peak (3) = peak (5)							3–5	1.72	2.32	
3d	Intensity, width							1–4	0.53	1.48	
	peak (2) = peak (5)	−0.21	0.34	0.24	1.27	2.28	2.90	3–6	1.57	2.66	1.30
	peak (3) = peak (6)							2–5	1.31	1.94	

[a] IS and QS (mm sec^{-1}).

temperatures of reduction also differed markedly from that of Catalyst A. This is shown in Fig. 3. The spectrum of Catalyst C initially prepared (Fig. 3a) showed only ferric ions (IS = 0.53 ± 0.02 mm sec^{-1}, QS = 0.95 ± 0.4 mm sec^{-1}) and was nearly identical to the spectrum of untreated Catalyst A (Fig. 1a). In contrast to Catalyst A, however, exposure of Catalyst C to hydrogen at *room temperature* converted much of the iron to the ferrous state (Fig. 3b). Although we did not make rate measurements it was clear by observing the Mössbauer spectrum immediately after the exposure to hydrogen and after several hours that the reduction was rapid being complete in less than 10 min.

Evacuation of Catalyst C for 1 hr at 500°C followed by 4 hr hydrogen reduction at the same temperature [Catalyst C-500] gave Fig. 3c. Ferrous ions were still present as indicated by the broad peak at ~2.4 mm sec^{-1} but the much larger intensity of the peak at ~0.3 mm sec^{-1} indicates that additional peaks were present in this velocity region. This is evident by comparing Fig. 1c and 3c for Catalysts A-500 and C-500, respectively. There was no evidence for ferromagnetic iron in Catalyst C-500.

Spectrum 3c was computer analyzed for 5 and 6 peaks. In each case two constrained ferrous doublets were used and a third iron species was assumed to be a singlet or doublet. In addition, both possible peak combinations for the ferrous doublets were investigated. A six-peak analysis of spectrum 3c gave nonphysical results in that the linewidths of one ferrous doublet were smaller than could possibly be obtained with our spectrometer. A five-peak analysis, assuming a single peak for a third iron species gave satisfactory linewidths for all peaks and the parameters shown in Table 2. Regardless of the peak combinations assigned to the constrained ferrous doublets this analysis indicated, in addition to the two ferrous doublets, an iron species with an IS of 0.28–0.29 mm sec^{-1} and a linewidth of 0.73 mm sec^{-1}. The large value of χ^2/df indicates a poor fit to the data, however.

The oxidation–reduction behavior of Catalyst C-500 at 25°C was the same as that observed for Catalyst C-700. This is shown in Fig. 3d and e. Computer analysis of spectrum 3d for six peaks with two constrained ferrous doublets gave the results shown in Table 2. The oxygen exposure produced peaks at −0.21 and 1.27 mm sec^{-1} which are nearly identical to the positions of the ferric peaks formed in oxidized Catalyst C-700 (Fig. 2b). These ferric peaks were removed when the oxidized sample was evacuated and exposed to hydrogen at 25°C (Fig. 3e) and a spectrum similar to that of the original 500°C reduced sample was again obtained. The behavior of Catalyst C-500 thus paralleled that of the same material reduced at 700°C.

Catalyst D (Physical Mixture, 0.05 wt% Fe/η-Al_2O_3 + 2.37 wt% Pd/η-Al_2O_3)

The Mössbauer spectra for Catalyst D were qualitatively similar to those of Catalyst C. Quantitatively, however, much less of the iron in Catalyst D could be converted to the species observed in Catalyst C for a given treatment. This is shown in Figs. 4 and 5. For Catalyst D-700 (Fig. 4a) computer analysis for 5 peaks with two constrained ferrous doublets gave a peak at 0.37 ± 0.02 mm sec^{-1} in addition to the two ferrous doublets. The agreement between this value and that observed for the main peak in Catalyst C-700 suggests that the same iron species was present in both materials.

To pursue this interpretation the sample giving spectrum 4a was exposed first to oxygen and then to hydrogen at 25°C with the results shown in Fig. 4b and c. The arrows in Fig. 4b indicate the locations of the ferric species observed in Catalyst C-700 after oxidation at room temperature. The decrease in intensity of the main peak at 0.37 mm sec^{-1} and the appearance of a small peak at 1.25 mm sec^{-1} suggests that a similar ferric species was also present when Catalyst D-700 was oxidized. Addition of hydrogen to this oxidized material removed the peak at ~1.25 mm sec^{-1} (Fig. 4c) and produced a spectrum similar to Fig. 4a of the original reduced material.

The behavior of Catalyst D at lower temperatures of reduction is shown in Fig. 5. Evacuation of Catalyst D followed by exposure to hydrogen all at room temperature gave Fig. 5a. The small peak at ~2.2 mm sec^{-1} and the asymmetry in the two peaks at lower velocities clearly indicates that some reduction to ferrous ions resulted from the hydrogen treatment. The extent

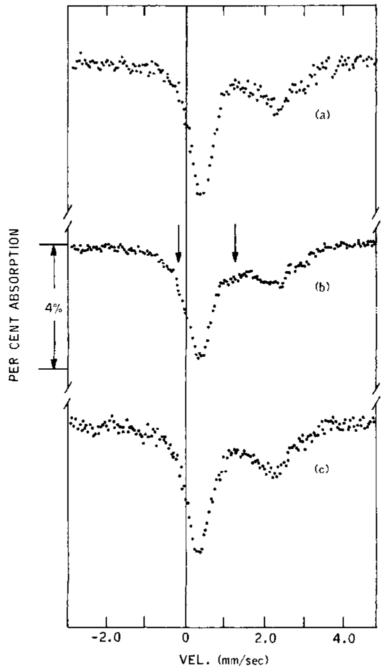

FIG. 4. Mössbauer spectra of Catalyst D (physical mixture, 0.05 wt% Fe, 2.37 wt% Pd/η-Al_2O_3). (a) Reduced H_2, 2 hr, 700°C; (b) exposed to O_2, 25°C; (c) exposed to H_2, 25°C.

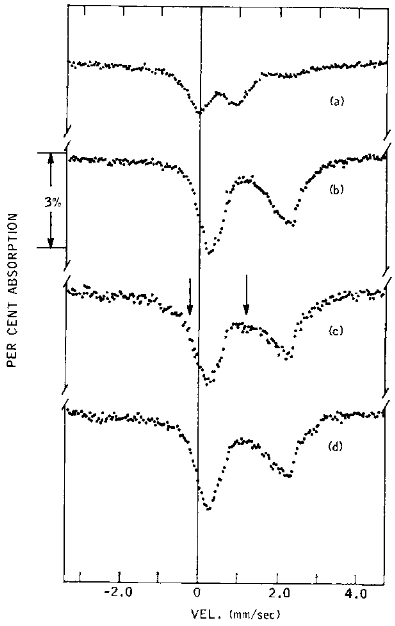

FIG. 5. Mössbauer spectra of Catalyst D (physical mixture, 0.05 wt% Fe, 2.37 wt% Pd/η-Al_2O_3). (a) Exposed to H_2, 25°C; (b) evacuated 1 hr, 500°C, reduced H_2, 4 hr, 500°C; (c) exposed to O_2, 25°C; (d) exposed to H_2, 25°C.

of reduction to ferrous ions in Catalyst D did not increase with time of exposure to hydrogen.

Evacuation of Catalyst D for 1 hr at 500°C followed by hydrogen reduction for 4 hr at the same temperature gave Fig. 5b. Qualitatively, spectrum 5b is similar to that of Fig. 1c for Catalyst A-500. Quantitatively, however, the ratio of the intensity of the left to the right peak is greater in spectrum 5b than in spectrum 1c and suggests that an additional iron species was present in Catalyst D-500. Since this species gave rise to an intensity small compared to the intensities of the ferrous peaks in the same velocity range, the peak or peaks due to the species could not be confidently resolved by computer analysis.

Exposure of Catalyst D-500 to oxygen and then to hydrogen at 25°C gave Fig. 5c and d. The arrows in Fig. 5c again show the positions of the ferric peaks observed previously for Catalyst C (Fig. 3d) and it is apparent that peaks were also produced in these positions in Catalyst D. Furthermore, these ferric peaks were removed when hydrogen was added to the sample at room temperature (Fig. 5d).

Dispersion Measurements on Catalyst C

The dispersion of Catalyst C was determined by Aben's method (*11*) for the same reduction treatments used in the Mössbauer experiments. These values are shown in Table 3. The particle sizes given in Table 3 were calculated from the chemisorption data assuming cube shaped crystallites with six surfaces exposed to the hydrogen and an area of 7.6 Å^2 (Pd atom)$^{-1}$. The small amount of iron in the catalyst was ignored in these calculations.

TABLE 3
DISPERSION MEASUREMENTS ON CATALYST C
(0.05 wt% Fe, 2.2 wt% Pd/η-Al_2O_3)

Treatment	H/M	Calculated particle size (Å)
Evacuated 1 hr, 500°C		
H_2 reduced 4 hr, 500°C	0.32	35
H_2 reduced 2 hr, 700°C	0.12	100

DISCUSSION

Catalyst A (0.05 wt% Fe/η-Al_2O_3)

The Mössbauer spectra of Catalyst A did not provide any evidence for metallic iron formation for reduction temperatures up to 700°C. Ferromagnetic iron metal if present in high enough concentration would have given a characteristic six-line magnetic hyperfine spectrum (*13*) which we did not observe. The initial catalyst which contained only ferric ions was unaffected by hydrogen at 25°C and only ferrous ions were detected on reduction at 500 or 700°C. Similar results were obtained by Sancier and Inami (*4*) on the basis of ESR studies although these authors suggested that some reduction to metallic iron occurred at 750°C. The sensitivity of the ESR technique is $\sim 10^6$ higher than that of the Mössbauer technique and thus we cannot rule out completely the possibility of some metallic iron formation at high reduction temperatures.

The formation of ferrous ions on reduction of alumina supported iron catalysts has been reported in several previous investigations (*14*, *15*). In general only ferrous ions are formed in reduced samples at low iron concentrations; whereas metallic iron appears, in addition to ferrous ions, with increasing iron concentration. This suggests that sites exist on η-Al_2O_3 which are capable of strongly complexing ferrous ions up to a certain concentration and preventing complete reduction. Once these sites are saturated additional iron can be reduced to the metallic state. Based on the available data it is difficult to determine in detail the nature of the ferrous ions formed in reduced Catalyst A. One possibility is suggested by the work of La Jacono, Schiavello and Cimino (*16*) who reported the formation of a "surface spinel," $NiAl_2O_4$, in NiO/Al_2O_3 catalysts. These authors concluded that the average thickness of the surface spinel phase was too small to be detected by X-ray diffraction techniques and that Ni^{2+} ions occupied both tetrahedral and octahedral sites. It seems reasonable that a similar surface spinel phase is formed in reduced Fe/η-Al_2O_3 catalysts.

Evidence for Alloy Formation in Palladium-Containing Catalysts

A comparison of the Mössbauer spectra of Catalyst A with those of Catalysts C and D shows clearly that the chemical nature of the iron is altered by the presence of palladium. Ostensibly the effect of palladium is to decrease the amount of iron which remains in the ferrous state after high temperature reduction and produce a new iron species. The reduction of Catalyst C at 700°C removed nearly all of the ferrous ions and gave a fairly "clean" Mössbauer spectrum. We shall, therefore, first consider the nature of the iron species formed in Catalyst C reduced at 700°C.

The IS of the main peak in Catalyst C-700 is 0.34 ± 0.01 mm sec^{-1}. This value is in excellent agreement with the IS of 0.33 ± 0.01 mm sec^{-1} reported for ^{57}Fe in dilute concentrations in bulk PdFe alloys (*17*). This latter value, however, pertains to the hydrogen-free alloy. The spectrum of Catalyst C-700 was recorded at 25°C with the sample in 1 atm of hydrogen. Under these conditions the palladium particles would be saturated with hydrogen. Alloying of all the iron with all of the palladium in Catalyst C would give an average alloy composition of 4.2 at.% Fe. Phillips and Kimball (*18*) have investigated Pd–Fe–H alloys at iron concentrations of 2 and 5 at.%. For the α-phase (containing little or no hydrogen) of *both* alloys they found a single line with an IS of 0.33 ± 0.003 mm sec^{-1} at 27°C. For the hydrogen saturated bulk alloys (β-phase) a single absorption line was also obtained but with an IS of 0.37 ± 0.003 mm sec^{-1}. The IS thus increases by 0.04 mm sec^{-1} on going from the hydrogen-free to the hydrogen-saturated bulk alloys. The IS of 0.34 ± 0.01 mm sec^{-1} for Catalyst C-700 is still compatible with an assignment to iron in palladium, however, since Aben (*11*) has shown that the hydrogen content of the β-phase is smaller for ~130 Å palladium particles than for the bulk material. Since the particle size in Catalyst C-700 was ~100 Å we expect the IS for iron in these particles to lie between 0.33 and 0.37 mm sec^{-1} as was observed.

The dispersion of Catalyst C after reduction at 700°C was 12% as determined by hydrogen chemisorption. Thus for homogeneous PdFe particles ~12% of the iron atoms would be on the surface of the PdFe particles. Exposure of the sample to oxygen should, therefore, oxidize those iron atoms on or near the surface without strongly affecting the iron atoms in the interior of the particles. The oxygen adsorption studies on Catalyst C-700 were consistent with such a model. Oxygen adsorption clearly affected some of the iron atoms (Fig. 2b) but a central peak with IS of 0.32 ± 0.01 mm sec^{-1} was still present in the oxidized sample. This peak we assign to iron atoms which are in the interior of the PdFe particles and are unaffected by oxygen. The doublet produced by the oxygen adsorption has an IS typical of high spin ferric ions. The QS of these ferric ions is quite large but this may be expected for surface ferric ions. Assuming that the recoil-free fraction for the ferric ions at the surface is the same as that of the iron atoms inside the palladium, the dispersion can be determined from the spectral area of the two species. This calculation gives for Catalyst C-700 a dispersion of 38% which is much larger than that determined by chemisorption. This suggests that the assumption of equal recoil-free fractions is not reasonable and that ferric ions are more strongly bound than iron atoms inside the palladium particles. It is also possible that oxygen adsorption affects not only iron atoms on the surface of the PdFe particles but also iron atoms one or two layers below the surface. This question will be pursued in subsequent investigations (*19*).

The iron in Catalyst C-700 which was oxidized at 25°C could also be re-reduced in hydrogen at the same temperature. Thus the oxygen which is adsorbed on the PdFe particles can be titrated by hydrogen at room temperature with removal of most of the oxygen from both palladium and iron. Since the Pd/Fe ratio for Catalyst C is ~23 each iron atom, whether on the surface or in the interior of the face-centered cubic palladium lattice, should have only palladium nearest neighbors. For this situation the iron–oxygen bond is apparently weakened to the point where the oxygen can be removed by hydrogen at 25°C. The reversible oxidation and reduction of iron at room temperature we take as indicative of iron which is associated with palladium. This contention is supported by recent studies by Bartholomew and Boudart (*20*) who have observed similar behavior for iron alloyed with platinum in carbon-supported PtFe catalysts. Metallic iron particles separated from the palladium by many particle diameters would be expected to oxidize at room temperature but not to undergo reduction back to the metallic state.

On the basis of the Mössbauer parameters for Catalyst C-700 and the reversible oxidation–reduction behavior of the iron in this material at room temperature we conclude that palladium–iron alloy particles were present. We found no evidence for metallic iron not associated with palladium and no other assignment appears to provide as consistent an explanation for the results.

The Mössbauer spectra for Catalyst C reduced at 500°C showed behavior similar to that observed for Catalyst C-700. The differences were primarily one of degree rather than nature of iron species formed. For Catalyst C-500 the ferrous peaks complicated the computer analysis and made determination of the Mössbauer parameters for the peaks near $\sim$0.3 mm sec^{-1} less accurate. It is clear, however, that reduction of Catalyst C at 500°C produced an iron species with an IS close to that observed for Catalyst C-700 and that this iron species underwent reversible oxidation in oxygen and reduction in hydrogen at room temperature. Furthermore, the Mössbauer parameters of the ferric species in Catalyst C-500 exposed to oxygen were identical to those observed in Catalyst C-700. These similarities, therefore, lead us to conclude that PdFe alloys were formed in Catalyst C at both reduction temperatures.

The PdFe particles in Catalyst C-500 differed from those in Catalyst C-700 in that the dispersion of the latter was only 12% compared to 32% for the former. For homogeneous alloy particles a larger fraction of the iron would occupy surface sites in the sample with the larger dispersion. This difference in Catalysts C-500 and C-700 is clearly evident from the spectra of the room temperature oxidized samples. The area under the ferric peaks for oxidized Catalyst A-500 was 2.2 times the area of the ferric peaks in oxidized Catalyst A-700. Since the experiments at 500 and 700°C were all carried out *in situ* on the same sample the areas for the respective peaks could be directly compared. The decrease in area under the ferric peaks from Catalyst C-700 to Catalyst C-500 agrees reasonably well with the 2.7-fold decrease in dispersion as determined by H_2 chemisorption.

The Mössbauer spectra of Catalyst D (physical mixture) reduced at 500 or 700°C were qualitatively the same as those observed for Catalyst C. In Catalyst D reduction at 500 or 700°C produced an iron species which underwent reversible oxidation in oxygen and reduction in hydrogen at room temperature. It appears that room temperature oxidation led to the same ferric species observed in Catalyst C. In addition, reduction of Catalyst D at 700°C produced a peak with an IS of 0.37 ± 0.02 mm sec^{-1} which, in view of the difficulty of resolving the spectrum, is in good agreement with the value observed for Catalyst C-700. It appears, therefore, that even in a physical mixture some iron was alloyed with palladium. The efficiency of the reduction and hence of the alloy formation was greatly reduced in the physical mixture compared to the sequentially impregnated Catalyst C.

The Role of Hydrogen Spillover in Alloy Formation

In this section we shall consider whether the present results provide any evidence that hydrogen migration over the support is important in alloy formation. Since the results of the room temperature hydrogen reduction of *fresh* Catalysts C and D are pertinent to this discussion they will be considered in this section.

There are two important models which must be considered to explain the formation of alloys in supported PdFe catalysts. In the first model actual contacts between palladium and iron oxide particles are required to facilitate the reduction. Hydrogen spillover does occur but only across the interfacial contacts between the palladium and the iron oxide. In the second model the palladium and iron oxide particles are separated by distances large compared to the particle diameters. Hydrogen is dissociated by the palladium and migrates over the support to the iron oxide particles where reduction occurs. At elevated temperatures the iron is reduced to the metal and diffuses over the support until contact with a palladium particle is made and alloy formation occurs. We shall now consider these models in view of the results of this investigation.

The formation of ferrous ions in fresh Catalysts C and D on exposure to hydrogen at 25°C clearly demonstrates the catalytic effect of palladium since Catalyst A was unaffected by this treatment. In terms of the second model described above this requires that *hydrogen migration occur over the Al_2O_3 surface at 25°C*. There are, however, theoretical and experimental arguments against this possibility. It seems clear from arguments which have been presented previously by Neikam and Vannice (*21*) and by Levy (*22*) that the desorption of hydrogen atoms from palladium into the gas phase cannot account for the reduction of Catalyst C at 25°C. Levy (*22*) has recently carried out a thermochemical analysis of hydrogen spillover in a number of systems. He concludes that hydrogen migration over a surface which separates a metal capable of dissociating hydrogen from an acceptor which is reduced can occur at 25°C only if a cocatalyst, e.g., H_2O, to solvate the proton and a conducting path to transport the electron are available. For Catalyst C titration of the oxygen covered palladium surface on exposure to hydrogen at 25°C would provide about 62 μmoles H_2O (g cat.)$^{-1}$ which would be sufficient to transport the hydrogen required for the one-electron reduction of the 9 μmoles Fe (g cat.)$^{-1}$. However, if the palladium and iron oxide particles in Catalyst C were separated by many particle diameters the electron could not be transported due to the poor electronic conductivity of the alumina support (*23*). If, however, the iron oxide particles were in contact with the palladium particles hydrogen migration need take place only across the interfacial contacts and the electron is injected directly into the acceptor. In this case water from the titration of the palladium may still participate and, indeed, may be necessary in the transport of hydrogen across the interfacial contacts.

Experimental evidence also indicates that hydrogen spillover requires direct contact between the metal which dissociates hydrogen and the acceptor in the absence of a conducting path between the two. Neikam and Vannice (*24*), for example, found that no hydrogen spillover occurred onto Al_2O_3 in a 0.5% Pt/Al_2O_3 even in the presence of organic molecules known to facilitate spillover in other systems. Novak and Koros (*2*) found that H_2PtCl_6 but not $Pt(NH_3)_2(NO_2)_2$ synergetically enhanced the activity of an alumina supported nickel catalyst for *n*-heptane hydrogenolysis. Charcosset *et al.* (*25*) subsequently observed that NiO strongly adsorbed platinum as H_2PtCl_6 but not as $Pt(NH_3)_2(NO_2)_2$. These results suggest that the inability of the latter to catalyze the reduction of NiO in NiO/Al_2O_3 catalysts was due to the absence of contacts between the platinum and the NiO whereas H_2PtCl_6 was effective because it was adsorbed on the NiO and catalyzed reduction to metallic nickel.

On the basis of the arguments presented above we conclude that the room temperature reduction of fresh Catalysts C and D resulted from contacts between palladium particles and iron oxide particles. The fact that the extent of reduction of physically mixed Catalyst D was much less than that of Catalyst C and did not increase with long exposure times to hydrogen is also consistent with a model involving contacts. The probability of palladium–iron oxide contacts and hence of reduction should be much greater in sequentially impregnated Catalyst C than in physically mixed Catalyst D as we observed.

The present investigation provides convincing evidence that reduced PdFe/Al_2O_3 catalysts prepared in the same manner as those of Sancier and Inami (S&I) contain most of the iron in the form of PdFe alloy particles. Ferrous ions were the only other chemical state of iron detected and no evidence for ferromagnetic iron was obtained from Mössbauer spectroscopy. As was pointed out in the introduction bulk PdFe alloys give an ESR signal with $g = 2.10$ which is the same as that for dispersed iron metal. If dispersed PdFe particles on Al_2O_3 give this same ESR signal then any ferromagnetic iron signal from the catalysts investigated by S&I would have been obscured by the dominant signal from PdFe. The question which must now be considered is whether or not the ESR signal observed by S&I can be attributed to PdFe alloy particles.

The ESR signal intensity from a given number of ESR active species is proportional to the net magnetization of the sample (*26*). For ferromagnetic materials at temperatures well below the Curie point the magnetization is $\sim 10^4$ times that of paramagnetic materials so that much larger ESR signal intensities are expected for ferromagnetic than for paramagnetic substances. As the temperature of a ferromagnetic material is increased to the Curie point and above the spontaneous magnetization and the ferromagnetic resonance signal disappear (*26*, *27*). This behavior is identical to that observed by S&I for the $g = 2.10$ resonance from a 0.5% Pd, 0.01% Fe/CaY catalyst. Temperature dependence studies of the ESR signal intensity were consistent with an assignment of the signal to a ferromagnetic center with a Curie temperature of 520°K. Alloying of all the metals in the PdFe/CaY catalyst would correspond to an average iron composition of ~3.7 at.% which is nearly identical to the average composition of Catalyst C of the present investigation. The Curie temperature of a bulk PdFe alloy of this composition is only ~100°K (*28*) and in the presence of hydrogen the β-hydride phase of the alloy is formed further decreasing the Curie temperature to <10°K (*18*). It seems clear, therefore, that PdFe particles with compositions corresponding to the Pd/Fe ratios for Catalyst C and the PdFe/CaY catalyst investigated by S&I could not have given the observed ESR signals at room temperature and above.

Since the Curie temperature of PdFe alloys increases with Fe concentration the presence of PdFe particles with significantly larger Fe concentrations than those corresponding to the Pd/Fe ratios in the catalysts could account for observations of S&I. For 25 at.% Fe in Pd Curie temperatures from 500 to 513°K have been reported (*29*) and these values are close to that observed by S&I for PdFe/CaY. At this composition hydrogen is not absorbed by the alloy and thus has no effect on the Curie temperature (*28*). Although the Mössbauer technique is sensitive to all the iron in Catalyst C it does not provide information on the extent to which the palladium is alloyed with the iron. Incomplete alloying of all the palladium in Catalyst C-500 would allow formation of PdFe particles with significantly larger iron concentrations than 4.2 at.%. In addition, a distribution in the particle size of the palladium and the amount of iron which comes in contact with an individual palladium particle during the catalyst preparation could lead to some PdFe particles with large Fe concentrations. At room temperature bulk PdFe alloys with iron concentrations greater than ~15 at.% Fe are ferromagnetic (*28*). We found no evidence, however, for ferromagnetic iron at room temperature in Catalyst C reduced at 500°C. This may indicate that PdFe particles with iron concentrations > ~15 at.% Fe were present in such small concentrations as to escape detection by Mössbauer spectroscopy. Such particles, however, would be detectable by the more sensitive ESR technique. It is also possible that ferromagnetic PdFe particles were present in detectable concentrations but small enough to exhibit superparamagnetic behavior at room temperature and give the paramagnetic Mössbauer spectrum observed for Catalyst C. In either case the important feature is that some PdFe particles be present in the reduced catalysts with sufficient iron concentrations to give rise to the ferromagnetic behavior observed by S&I.

We cannot rule out completely the possibility that the ESR signals with $g = 2.10$ observed by S&I were indeed due to ferromagnetic iron metal particles present in such small concentrations that they escaped detection by Mössbauer spectroscopy. In this case no ferromagnetic PdFe particles would be required. It is clear from the present investigation, however, that for this situation the ESR technique would not identify the chemical states of the major portion of the iron in the catalyst but would detect only a minor iron component.

We prefer an explanation based on the formation of PdFe alloy particles to rationalize the results of S&I. For PdFe alloys the Curie temperature of 520°K observed for PdFe/CaY need not be rationalized in terms of a lowering of the Curie point of iron due to particle size but to the formation of some PdFe alloy particles with iron concentrations of ~25 at.%. It is interesting to note that palladium and iron form an ordered compound of this composition, i.e., Pd_3Fe. The existence of this ordered compound could favor its formation in the supported PdFe catalysts.

CONCLUSIONS

Mössbauer spectroscopic studies of PdFe/η-Al_2O_3 reduced at 500 or 700°C and of the room temperature oxidation–reduction behavior of the iron in the reduced catalysts show that PdFe alloy particles are present. No evidence for the formation of unalloyed ferromagnetic iron in the reduced catalysts was obtained. This investigation supports a model in which actual contacts between palladium particles and an oxide of iron are required to facilitate reduction of the iron and formation of an alloy. Hydrogen spillover does occur but is a short range phenomenon involving diffusion of hydrogen only across the interfacial contacts between palladium and the iron oxide which is reduced. It appears unlikely that migration of hydrogen over the surface of the support is important in reducing the iron.

This investigation has much broader implications. It demonstrates that ^{57}Fe can effectively be used as a chemical probe of supported metal catalysts and greatly extends the scope of the application of Mössbauer spectroscopy in heterogeneous catalysis.

ACKNOWLEDGMENTS

We are grateful to H. W. Dougherty and R. J. Traina for assistance in conducting the experiments reported in this paper. One of us (R. L. G.) acknowledges helpful discussions with Drs. R. B. Levy and M. A. Vannice concerning hydrogen spillover.

REFERENCES

1. ROMAN, A., AND DELMON, B., *C. R. Acad. Sci., Ser. C* **273,** 1310 (1971); ROMAN, A., AND DELMON, B., *J. Catal.* **30,** 333 (1973).
2. NOVAK, E. J., AND KOROS, R. M., *J. Catal.* **7,** 50 (1967).
3. NOVAK, E. J., *J. Phys. Chem.* **73,** 3790 (1969).
4. SANCIER, K. M., AND INAMI, S. H., *J. Catal.* **11,** 135 (1968).
5. BAGGULEY, D. M. S., *Proc. Roy. Soc., Ser. A* **228,** 549 (1955).
6. BAGGULEY, D. M. S., AND ROBERTSON, J. A., Phys. Lett. **27A,** 516 (1968); BAGGULEY, D. M. S., CROSSLEY, W. A., AND LIESEGANG, J., Proc. Phys. Soc. **90,** 1047 (1967).
7. DELGASS, W. N., AND BOUDART, M., *Catal. Rev.* **2,** 129 (1968).
8. COSGROVE, J. G., AND COLLINS, R. L., *Nucl. Instrum. Methods* **95,** 269 (1971).
9. DURE, B. J., AND GIBB, T. C., *J. Chem. Soc. A* 1478 (1967).
10. DIXON, W. J., AND MASSEY, F. J., "Introduction to Statistical Analysis," 2nd ed., p. 386. McGraw-Hill, New York, 1957.
11. ABEN, P. C., *J. Catal.* **10,** 224 (1968).
12. GREENWOOD, N. N., AND GIBB, T. C., "Mössbauer Spectroscopy," p. 91. Chapman and Hall, London, 1971.
13. PRESTON, R. S., HANNA, S. S., AND HERBERLE, J., *Phys. Rev.* **128,** 2207 (1962).
14. HOBSON, M. C., JR., AND GAGER, H. M., *Proc. Int. Congr. Catal., 4th (Moscow) 1968* (pap. 48).

15. Holbert, H., and Arnold, D., *Proc. Conf. Appl. Mössbauer Effect (Tihany, Hungary) 1969,* p. 325.

16. La Jacono, M., Schiavello, M., and Cimino, A., *J. Phys. Chem.* **75,** 1044 (1971).

17. Qaim, S. M., *Proc. Phys. Soc.* **90,** 1065 (1967).

18. Phillips, W. C., and Kimball, C. W., *Phys. Rev.* **165,** 401 (1968).

19. Garten, R. L., unpublished data.

20. Bartholomew, C. H., and Boudart, M., *J. Catal.* **29,** 278 (1973).

21. Neikam, W. C., and Vannice, M. A., *J. Catal.* **27,** 207 (1972).

22. Levy, R. B., PhD dissertation, Stanford Univ., 1972.

23. Vannice, M. A., and Neikam, W. C., *J. Catal.* **20,** 260 (1971).

24. Neikam, W. C., and Vannice, M. A., *Proc. Int. Congr. Catal., 5th* **1,** 621 (1972).

25. Charlosset, H., Frety, R., Soldat, A., and Trambouze, Y., *J. Catal.* **22,** 204 (1971).

26. Slinkin, A. A., Russ. Chem. Rev. **37,** 642 (1968).

27. Loy, B. R., and Noddings, C. R., *J. Catal.* **3,** 1 (1964).

28. Carlow, J. S., and Meads, R. E., *Proc. Phys. Soc., London (Solid State Phys.)* **2,** 2120 (1969).

29. Longworth, G., *Phys. Rev.* **172,** 572 (1968).