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Surface Composition and Chemistry of Supported Platinum–Iron Alloys

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Mössbauer spectroscopy and chemisorption data involving H_2 and O_2 have been used in a complementary manner to determine the surface composition of carbon-supported platinum-iron alloys. Surface iron was determined from the relative Mössbauer spectral area of surface components compared to the total spectral area, and the total metal dispersion by hydrogen titration. The surface composition for reduced samples exposed to hydrogen at room temperature was determined to be substantially the same as the nominal metal bulk composition. No change in surface composition occurred after exposure of the sample to air at room temperature; however, iron enrichment of the surface occurred after a 10-min exposure to air at 300°C.

Metals used as catalysts are frequently in the form of small crystallites (10–100 Å in diameter) dispersed on a supporting material such as silica, alumina, or carbon. Two major problems arise in the study of supported metal alloys (*a*) the determination of the total dispersion D_T of the metal defined as the number of surface metal atoms divided by the total number of metal atoms in the sample and (*b*) the determination of surface composition which may differ from bulk composition (*1–8*).

The vast majority of previous catalytic investigations of alloys has involved low surface-area forms such as powders, foils, wires or films. Only four papers have appeared thus far in which supported alloys were studied (*1–3, 9*). Prior to this study there has been no investigation of supported platinum–iron alloys although the bulk platinum–iron alloy system has received considerable attention (*14–19*). The iron–platinum alloy system is of natural catalytic interest because of the wide application of iron and platinum catalysts. The preparation of platinum–iron catalysts with crystallites having average diameters of 20–30 Å was reported in an earlier communication (*9*). This paper reports the complementary use of chemisorption and Mössbauer spectroscopy in an attempt to determine surface composition of these supported catalysts. Recent reviews describe the application of Mössbauer spectroscopy to the study of surface phenomena (*10, 11*) and catalysis (*12, 13*).

EXPERIMENTAL

Catalyst Preparation

The preparation of 6 Pt–Fe alloys on graphitized carbon was carried out as described elsewhere (*9*). Their compositions are listed in Table 1. Analysis by atomic absorption spectroscopy (*14*) of the 12.1% Pt–Fe/C sample revealed 8.9% Pt and 2.7% Fe providing a good check of the values of 9.4% Pt and 2.7% Fe determined in the preparation by initial weighing of platinum and iron salts. A modification in the procedure for preparation of two 1.0%, a 1.8%, and a 9.4% Pt–Fe/C involved using Fe_2O_3 enriched in Fe^{57} for Mössbauer spectroscopy. Two analytical reagent grade

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TABLE 1

PLATINUM–IRON CATALYSTS SUPPORTED ON CARBON: COMPOSITION TOTAL DISPERSION D_T AND AVERAGE PARTICLE DIAMETER d

Weight % metal	Atomic % Fe	D_T %	d Å[a]
1.0	50	62	16
3.9	50	35	28
12.1	48	31	31
1.8	34	61	17
1.0	25	64	18
9.4	10	40	26

[a] Average particle diameters were calculated assuming spherical particles and average site densities for Pt and Fe of 8.4 and 9.4 Å²/atom, respectively.

samples of Fe_2O_3 (Oak Ridge National Laboratory) containing iron composed of 69.60% and 90.73% Fe^{57} were used in the preparation of these four catalysts. The iron oxide was dissolved in a 24-fold excess of concentrated HCl, and the solution was evaporated almost to dryness. Doubly-distilled water was added, and the solution was again evaporated. This was repeated twice or three times until the pH was about 3, at which point absolute ethanol was added to dissolve the iron chloride for removal to the ethanol–benzene impregnation solution. Analytical reagent grade chloroplatinic acid (Baker Analyzed, 99.95% and Roc/Ric Research 99.9%, ferric nitrate (Baker Analyzed, 99.4%) and benzene (Mallinckrodt) were used in the impregnation. A high purity, nonporous graphitized carbon known as Graphon with a BET surface area of 87 m²/g was obtained from the Cabot Corporation. Pretreatment of the carbon support in air at 600°C was described earlier (*9*).

A 50 atomic% iron in platinum foil was prepared by electroplating iron on to a 0.2-mil thick foil of platinum (Engelhard, 99.9%) and annealing at 1050°C in a quartz cell while flowing H_2 over the sample. The plating was carried out at −1.00 V versus a saturated calomel electrode in a plating solution prepared from 30 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 120 ml distilled water.

Gases

Hydrogen gas (Liquid Carbonic Corporation, 99.93%) was purified further by passing through a Deoxo catalytic hydrogen purifier (Engelhard) followed by a cold trap. Oxygen (Liquid Carbonic, 99.5%) was passed into a Pyrex storage bulb preceded by a zeolite trap cooled to 195K.

Equipment and Procedures

Mössbauer spectrometer. The fast-counting Mössbauer spectrometer system consisted of a velocity transducer (Austin Science Associates) driven in a constant-acceleration mode by integration and feedback electronics (ASA) slaved to a 512-channel multichannel analyzer (Nuclear Data 2200) used also to store counts as a function of velocity. The output signal of a Kr–CO_2-filled proportional-counter tube (Reuter-Stokes RG-61) was preamplified by a low-noise proportional-counter preamplifier (Canberra Industries 1406) and presented to a high-gain amplifier (CI 1431) followed by a dc restorer (CI 1414) and a fast-pulse height analyzer (CI 1431) to produce the appropriate count PHA signal input for the multichannel analyzer. A high voltage bias of 1650 V was supplied to the proportional counter by means of a 0–3000 V power supply (Hewlett-Packard, Harrison 6516A). The upper and lower discriminators of the pulse height analyzer were set by either oscilloscope or ADC (analogue to digital conversion) coincidence in which the PHA signal was routed through a logic shaper and delay (CI 1455). Absolute incremental velocities were determined for each channel of the multichannel analyzer by means of a helium laser interferometer calibration system (ASA). A teletype printer and tape punch (Teletype 33) and a point plotter (HP 7004B) served as data outputs for the system. The radioactive source, 100 mCi of Co^{57} in copper (New England Nuclear), exhibited an experimental natural line width of 0.24 mm/sec for a sodium nitroprusside absorber. Positive velocity corresponded to the source moving towards the absorber.

Absorber wafers, ¾ in. in diameter were prepared by compressing approximately 0.25 g of sample in a Carver press. Sample pretreatments and "in situ" Mössbauer experiments at high and low temperatures were carried out in two stainless steel water-jacketed vacuum cells designed for heating samples to 500°C, a metal liquid nitrogen dewar with furnace, and a metal liquid helium dewar with an inner sample chamber and furnace. In each of these cells, the vacuum tight transmission windows consisted of 10-mil thick beryllium discs (Kawecki Berylco Ind.) containing less than 50 ppm iron. Samples were held by stainless steel rings in cylindrical sample chambers of stainless steel or copper. Heating was accomplished by nichrome resistance windings within each cell, and temperature was monitored by a thermocouple located near the sample. A stainless steel bellows and o-ring connection enabled access of each cell to high vacuum and gas handling systems.

In order to facilitate calculation of spectral areas an estimate of nonresonant background in the 14.4 keV window of the proportional counter was made by counting at nonresonant velocities with a 4.5-mil brass foil between the absorber and detector (*15*). The data for each run were submitted to a least-squares fitting by a version of the Argonne variable metric minimization program for fitting Mössbauer data. Spectral areas were calculated from the fitted parameters for each peak and were corrected for the signal-to-noise ratio measured by the brass foil technique.

Other apparatus. X-ray diffraction was made with a Picker bi-planar diffractometer employing copper $K\alpha$ radiation. The volumetric apparatus for chemisorption measurements has been described elsewhere (*16*).

RESULTS

X-Ray Diffraction

X-ray diffraction patterns for samples of 3.9 and 12.1% Pt–Fe (50/50)/C (50/50 refers to respective atomic per cents of platinum and iron) were characteristic of the ordered tetragonal PtFe structure (*17–19*). The X-ray pattern for the 9.4% Pt–Fe 90/10)/C alloy indicated *d* values intermediate between those of ordered PtFe and platinum metal. The X-ray diffraction pattern for the 50 atomic% iron in platinum foil contained sharp lines all of which could be assigned to the ordered PtFe structure.

For all three samples reduced at 500°C the X-ray peaks were very broad indicating very small particles in the 30–40 Å range (*20*).

Mössbauer Spectra

Without exception the spectra for reduced supported alloys did not exhibit any detectable lines for metallic iron. Peak parameters such as intensity, width, and velocity were obtained by computer fitting each spectrum with different numbers of peaks from one to six. The criteria for selecting best fits and correct number of peaks were (a) minimization of the chi-squared value for each spectrum and (b) selection of physically meaningful parameters, e.g., line widths not less than 0.25 mm/sec and only positive values for width and intensity. Constrained fitting was used only in two cases: one in which the line width of the unconstrained fit of one peak of a quadrupole-split doublet was smaller than 0.25 mm/sec and the other in which the line widths of a quadrupole-split doublet differed greatly. By constraining the two peaks of the corresponding doublets to have equal widths, physically meaningful results obtained. The room-temperature spectra of Pt–Fe/C alloys prepared by reduction at 500°C were generally characterized by broad absorption envelopes which were best computer-fitted by two quadrupole-split doublets as illustrated by a typical fitted spectrum in Fig. 1. The outer, less-intense doublet having broad line widths was assigned to surface atoms whereas the inner doublet having smaller line widths and larger dips was assigned to bulk atoms.

All isomer shifts in this paper have reference to a Co^{57} in Fe source. The isomer shifts and line widths at 25°C of the inner

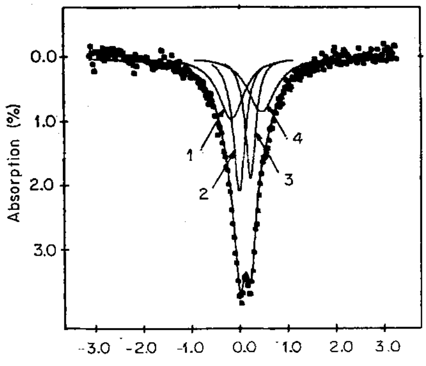

FIG. 1. Typical computer-fitted Mössbauer spectrum for Pt–Fe/C (corresponds to Fig. 6c). Peaks (1) and (4) form the outer surface doublet. Peaks (2) and (3) form the inner bulk doublet.

doublet for reduced alloy catalysts in one atmosphere of H_2 and for a Pt–Fe(50/50) foil are listed in Table 2 and compared with literature values for bulk Pt–Fe alloys. Excellent agreement is apparent between isomer shifts for 9.4% Pt–Fe(90)/10)/C and dilute iron in platinum and between isomer shifts for supported and bulk alloys containing 25, 34, and 50 atomic% iron. An isomer shift of 0.50 mm/sec (with respect to iron) was observed for 9.4% Pt–Fe(90/10)/C at 10K in excellent agreement with a value of 0.51 mm/sec at 4K for dilute iron in platinum (*21*). From the values in Table 2 it is evident that the isomer shift of iron in platinum decreases only slightly as the concentration of iron is increased from less than 1–50 atomic%. There appears to be no dependence of the isomer shift on particle size for the reduced metallic state. However, line widths are significantly larger for the catalyst samples compared to bulk alloys and become larger with increasing iron content.

Low-temperature spectra show a superparamagnetic lowering of the magnetic ordering temperature for all carbon-supported alloys compared to bulk alloys. The transition temperature is very sensitive to particle size as evidenced by data for samples of 50 atomic% iron in platinum in Table 3 in which approximate transition temperatures at which magnetic hyperfine splitting was observed are listed with average particle diameters determined from X-ray broadening (127 and 46 Å) or the Benson–Boudart titration (*16*). The Curie temperature obtained for 50 atomic% iron in platinum by extrapolation of hyperfine fields as a function of temperature to zero field in 733K in good agreement with a reported value of 753K (*24*). Also listed are hyperfine fields determined from the magnetic hyperfine splitting at 77K. The hyperfine fields at 77K are smaller than

TABLE 2

ISOMER SHIFTS AND LINE WIDTHS FOR Pt–Fe AT 25°C EXCEPT AS INDICATED

Sample	I.S. (mm sec^{-1})	Line width (mm sec^{-1})	Reference
Dilute Fe in Pt	0.36	0.30	*21*
Dilute Co^{57} in Pt	0.35		*22*
Dilute Fe in Pt	0.34		*23*
Same at 4K	0.51		*21*
9.4% Pt-Fe(90/10)/C	0.35	0.64	This work
Same at 10K	0.50		This work
24.0 atomic% Fe in Pt	0.32	0.43	*25*
1.0% Pt-Fe(75/25)/C	0.32	0.98	This work
34.5 atomic% Fe in Pt	0.29	0.68	*25*
1.8% Pt-Fe(66/34)/C	0.34	1.33	This work
50 atomic% Fe in Pt	0.31	mag. hyperfine splitting	This work
1.0% Pt-Fe(50/50)/C	0.305	1.56	This work
3.9% Pt-Fe(50/50)/C	0.285	1.53	This work
12.1% Pt-Fe(50/50)/C	0.32	1.58	This work

TABLE 3
PARTICLE SIZE d, MAGNETIC TRANSITION TEMPERATURE T_C, AND HYPERFINE FIELD H AT 77 K FOR 50 ATOMIC% IRON IN PLATINUM

Sample	d (A)	T_C (K)	H at 77 K (kOe)
Pt–Fe Foil	Bulk	733	293
12.1% Pt–Fe/C Reduced at 900°C	127	600	298
1.0% Pt–Fe/C Reduced at 900°C	46	500	298
12.1% Pt–Fe/C Reduced at 500°C	30	200	316
1.0% Pt–Fe/C Reduced at 500°C	16	20	—

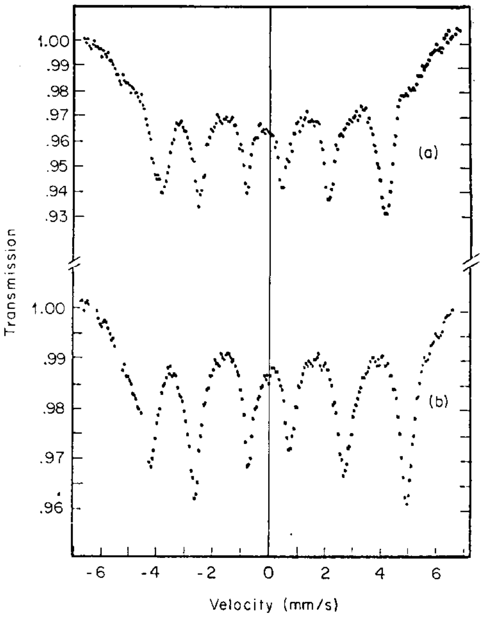

FIG. 2. Mössbauer spectra of 50% Fe in Pt (a) foil at 298K, (b) 1.0% Pt–Fe/C (reduced at 900°C, d = 46 Å at 77K.

for pure metallic iron and within the range of values, 288–310 kOe at 4.3K, reported for 24–34 atomic% iron in platinum (*25*). It appears that the hyperfine field at 77K increases slightly with decreasing particle size. No magnetic hyperfine splitting was observed at 77K for 1.0% Pt–Fe(50/50)/C reduced at 500°C (average particle diameter of 16 Å). At 10K a large magnetic splitting was observed, the spectrum consisting of two superimposed six-line spectra having hyperfine fields of 316 and 331 kOe.

The spectrum at 77K for a sample of 1.0% Pt–Fe(50/50)/C reduced at 900°C is compared in Fig. 2 with a spectrum at 298K for 50 atomic% iron in platinum foil. The line widths, shapes, intensities, and magnetic splittings are remarkably similar although the first sample contains very small alloy crystallites, and the second is a bulk alloy. Broadening of the lines in both cases is probably due to quadrupole interactions and the existence of two or more magnetic sites. The low-temperature Mössbauer spectra for 12.1% Pt–Fe(50/50)/C samples reduced at 500 and 900°C and for 1.0% Pt–Fe(50/50)/C reduced at 900°C are also very similar to those in Fig. 2.

No magnetic hyperfine structure was observed above or at 77K for carbon-supported alloys containing 34, 25, and 10% iron in platinum. At 10K there was extensive magnetic interaction observed for the 9.4% Pt–Fe/C sample (10 atomic% iron). The internal field was found to be 325 kOe compared to a value for pure iron at 4K of 342 kOe (*26*). The six broad lines for the supported alloy are very similar to spectra observed (*27*) for 1–13 atomic% iron in platinum, and the hyperfine field is the same as that expected for a bulk alloy containing 10 atomic% iron in platinum at 4K (*27*).

Effect of Chemisorption on Mössbauer Spectra

Marked changes in Mössbauer spectra at 25°C were observed as reduced, hydrogen covered Pt–Fe/C samples were exposed first to air or oxygen and then to hydrogen, both at room temperature. Treatment in oxygen at 300°C for 10 min produced even more significant changes. The room-temperature Mössbauer parameters for four different Pt–Fe/C catalysts following treatment of the reduced sample with one atmosphere of air and then one atmosphere of hydrogen at 25°C, and finally with 160 Torr of oxygen at 300°C for 10 min are presented in Table 4. The corresponding Mössbauer spectra for the same four catalysts are presented in Figs. 3–6. The spectra in Fig. 3 for the 1% Pt–Fe(50/50)/C

TABLE 4
ROOM-TEMPERATURE MÖSSBAUER PARAMETERS (IN MM/SEC) FOR Pt–Fe/C SAMPLES 1 ATM OF AIR, H_2, OR O_2

Sample	Pretreatment	Run condition	IS^{2-3}	IS^{1-4}	QS^{2-3}	QS^{1-4}	$\%D_{Fe}$
1.0% Pt–Fe/C (50 atomic% Fe)	Red. 5 hr., 400°C	H_2	0.305	0.325	0.423	0.987	54
	Exp. air, 25°C	air	0.360	0.357	0.689	1.149	57
	Exp. H_2, 25°C	H_2	0.381	0.390	0.682	1.128	52
	Exp. O_2, 300°C 10 min	O_2	0.377	0.365	0.763	1.239	79
1.8% Pt–Fe/C (34 atomic% Fe)	Red. 5 hr., 410°C	H_2	0.336	0.352	0.380	0.925	60
	Exp. air, 25°C	air	0.357	0.365	0.607	1.096	56
	Exp. H_2, 25°C	H_2	0.304	0.335	0.345	0.884	60
	Exp. O_2, 300°C 10 min	O_2	0.386	0.318	0.679	1.031	68
1.0% Pt–Fe/C (25 atomic% Fe)	Prev. Red., 11 hr., 500°C Red, 3 hr., 410°C	H_2	0.324	0.350	0.262	0.747	56
	Exp. air, 25°C	air	0.311	0.344	0.271	0.858	65
	Exp. H_2, 25°C	H_2	0.317	0.353	0.282	0.826	58
	Exp. O_2, 300°C 10 min	O_2	0.287	0.365	0.182	0.844	85
9.4% Pt–Fe/C (10 atomic% Fe)	Red. 7 hr., 470°C	H_2	0.349	0.449	0.245	0.732	47
	Evac. 2 hr., 560°C	Vacuum	0.349	—	0.247	—	—
	Exp. air, 25°C	air	0.336	0.372	0.226	0.682	53
	Exp. O_2, 300°C	O_2	0.329	0.330	0.221	0.928	72
	Exp. H_2, 25°C	H_2	0.316	0.358	0.189	0.785	52

are almost identical in appearance with spectra for the 12.1 and 3.9% Pt–Fe(50/50)/C samples treated under the same conditions although a better signal-to-noise ratio in the former enabled more quantitative analysis by computer fitting. Isomer shifts and quadrupole splittings were obtained by computer fitting each set of data with two doublets (see Fig. 1). Spectra obtained following titration of the air-exposed sample by hydrogen at 25°C were best fitted with an additional doublet positioned at a relatively large positive velocity. The spectrum of 9.4% Pt–Fe(90/10)/C after evacuation of the reduced sample at 560°C during two hours (Table 4 and Fig. 6) was best fitted with one inner doublet. The spectral area was less than for the reduced sample in one atmosphere of hydrogen.

If the recoil-free fraction for surface Fe atoms strongly bonded to chemisorbed species is the same as for interior atoms, the spectral area under the outer doublet is proportional to the number of Fe^{57} surface atoms and the total spectral area to all Fe^{57} atoms in the sample. The ratio of these two areas is a measure of iron dispersion D_{Fe} defined as the ratio of surface Fe atoms to total number of Fe atoms in the sample. Thus the values of D_{Fe} in Table 4 were calculated by taking the area under the outer "surface" doublet to total area determined by computer fitting. For spectra corresponding to reduced samples exposed to air and then titrated with hydrogen at 25°C, D_{Fe} was calculated by dividing the area under all outer "surface" peaks of the 6-line computer fit (exclusive of the two well-defined inner "bulk" peaks) by total area. Iron dispersion did not change significantly with temperature as evidenced by values of 67 and 62.8% obtained at 77K for reduced samples (evacuated at room temperature) of 1.0% Pt–Fe(50/50)/C and 1.0% Pt–Fe(75/25)/C. For the samples, the room temperature recoil-free fractions calculated for both inner and outer doublets and Debye temperatures calculated from the temperature recoil-free fractions calculated for in Table 5. According to these data the recoil-free fractions at 300K for 25 and 50 atomic% iron in platinum are the same for

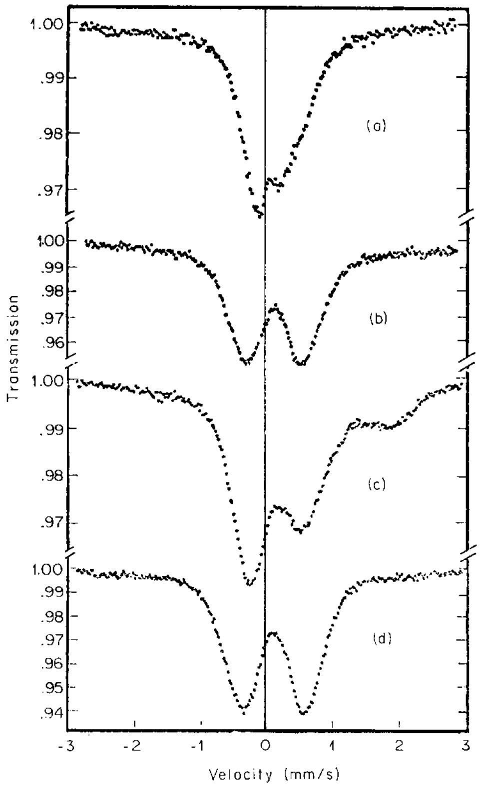

FIG. 3. Room temperature Mössbauer spectra for 1.0% Pt–Fe(50/50)/C. (a) After reduction in flowing hydrogen during 4 hr at 400°C and cooling at 25°C in hydrogen (1 atm). (b) After evacuation and exposure to air at 25°C. (c) After evacuation and exposure to hydrogen at 25°C (following exposure to air). (d) After exposure to oxygen (160 Torr) at 300°C, 10 min.

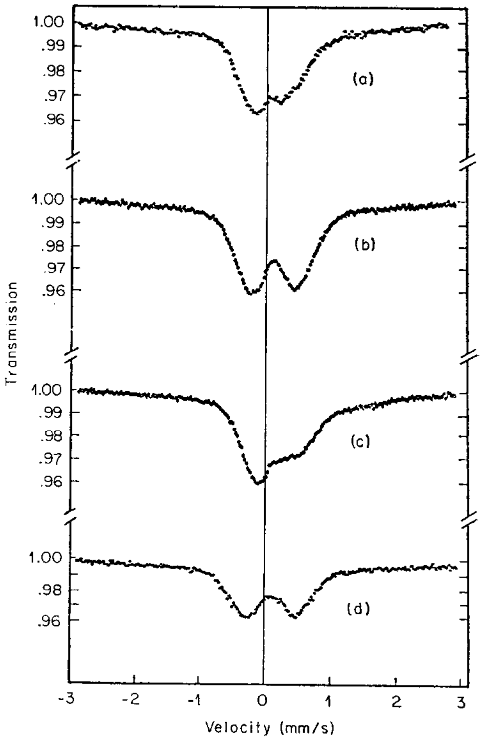

FIG. 4. Room temperature Mössbauer spectra for 1.8% Pt–Fe(66/34)/C. (a) After reduction in flowing hydrogen during 5 hr at 410°C and cooling to 25°C in hydrogen (1 atm). (b) After evacuation and exposure to air at 25°C. (c) After evacuation and exposure to hydrogen at 25°C (following exposure to air). (d) After exposure to oxygen (160 Torr) at 300°C, 10 min.

bulk and surface atoms upon which hydrogen is chemisorbed. However, the overall recoil-free fraction of the small particles (average diameter less than 20 Å) is a factor of five smaller than reported for dilute iron in platinum. The Debye temperatures for 1.0% Pt–Fe(50/50)/C are the same for bulk and surface atoms. For the 1% Pt–Fe(75/25)/C the Debye temperature is larger for bulk atoms. Both sets of Debye temperatures are lower than values of 420 and 225K reported for iron and platinum metals, respectively (*28*).

Exposure of reduced hydrogen-covered catalyst samples to one atmosphere of air (or 160 Torr of oxygen) at 25°C after room-temperature evacuation produced the following effects: (a) an increased quadrupole splitting of the outer doublet (the 9.4% Pt–Fe(90/10)/C catalyst excepted); (b) for 1% Pt–Fe(50/50)/C and 1.8% Pt–Fe(66/34)/C samples an increased quadrupole splitting of the inner doublet; (c) a decrease in the isomer shift of the outer doublet for 9.4% Pt–Fe(90/10)/C; (d) an increase in the isomer shift of the inner doublet for 1.0% Pt–Fe(50/50)/C. The increased quadrupolar broadening upon exposure to air is visually apparent in Figs. 3–6. Apparently the extent of broadening decreases with decreasing iron content of the catalyst.

Following the exposure to air, each sample was evacuated and then exposed to one atmosphere of hydrogen at 25°C. The resultant spectra generally demonstrated a

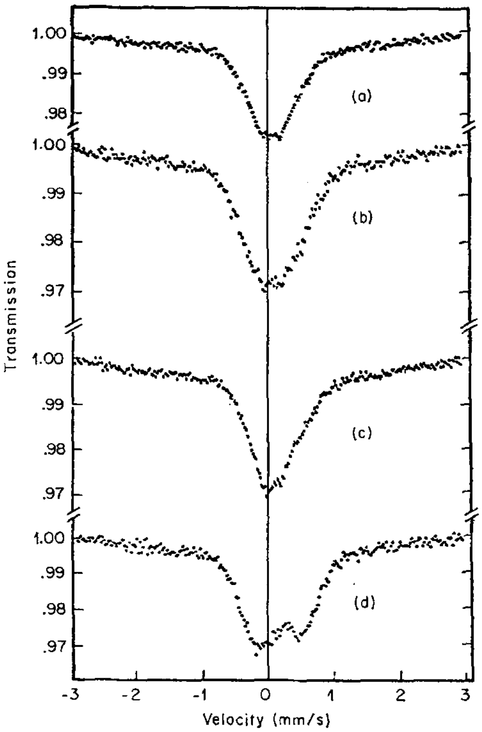

FIG. 5. Room-temperature Mössbauer spectra for 10% Pt–Fe(75/25)/C. (a) After reduction in flowing hydrogen during 11 hr at 500°C, evacuation and exposure to air at 25°C, reduction during 3 hr at 410°C, and cooling to 25°C in hydrogen (1 atm). (b) After evacuation and exposure to air at 25°C. (c) After evacuation and exposure to hydrogen at 25°C (following exposure to air). (d) After exposure to oxygen (160 Torr) at 300°C, 10 min.

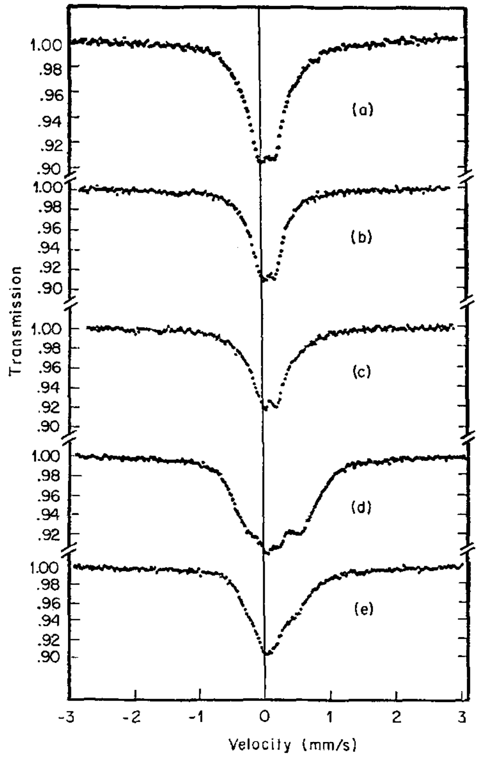

FIG. 6. Room-temperature Mössbauer spectra for 9.4% Pt–Fe(90/10)/C. (a) After reduction during 7 hr at 470°C in flowing hydrogen and cooling to 25°C in hydrogen (1 atm). (b) After evacuation during 2 hr at 560°C. (c) After exposure to air at 25°C. (d) After exposure to air at 300°C for 10 min. (e) After evacuation and exposure to hydrogen (1 atm) at 25°C.

significant positive shift in the spectral area and the appearance of a new doublet having a large positive isomer shift (for example see Fig. 3) the parameters for which are listed in Table 5 for 1.0% and 1.8% Pt–Fe/C samples. For the 1.0% Pt–Fe(50/50)/C spectrum the best fit (lowest chi-squared value) with five peaks included a singlet at 2.12 mm/sec (with respect to iron) whereas spectra of 1.8% Pt–Fe(67/34) and 1.0% Pt–Fe(75/25)/C were best fitted with 6 lines including a doublet at large positive velocity characteristic of Fe^{2+}. Nevertheless, the singlet at 2.12 mm/sec (with respect to iron) for the 50/50 alloy on carbon is undoubtedly the right portion of a Fe^{2+} doublet, the left

TABLE 5

RECOIL-FREE FRACTIONS f AND DEBYE TEMPERATURES θ_D FOR 1% Pt–Fe/C SAMPLES

Sample	Doublet	f (300 K)	θ_D (K)
1.0% Pt–Fe(50/50)/C	Inner (Bulk)	0.154	140
	Outer (Surface)	0.150	145
1.0% Pt–Fe(75/25)/C	Inner (Bulk)	0.159	197
	Outer (Surface)	0.163	158

TABLE 6

Parameters (in mm/sec) for Fe_2^+ Doublets$^{5-6}$ Observed in H_2 Titration of Oxygen Covered Pt-Fe/C Samples

Sample	QS$^{5-6}$	IS$^{5-6}$
1.0% Pt-Fe(50/50)/C	1.94	1.15
1.8% Pt-Fe(66/34)/C	0.96	1.52
1.0% Pt-Fe(75/25)/C	0.43	0.71

portion of which is apparently superimposed on the very broad positive portion of the outer surface doublet.

Treatments with air and hydrogen at 25°C generally did not affect the iron dispersion calculated from spectral areas of the inner and outer doublets. However, the treatment of catalyst samples at 300°C in 160 Torr oxygen for 10 min caused a shift in spectral area to the outer "surface" doublet and an increased quadrupole splitting of the outer doublet. The shift in spectral areas is most readily seen in Fig. 6 for 9.4% Pt–Fe(90/10)/C.

Chemisorption Measurements

Oxygen, hydrogen, and repeated oxygen uptakes were measured at room temperature for both 1.0 and 12.1% Pt–Fe(50 50)/C samples which had been reduced for 12 hr in one atmosphere of flowing hydrogen at 450°C. The data are listed in Table 7 along with the data for the same 12.1% Pt–Fe (50/50)/C sample after treatment at 300°C in 170 Torr of oxygen for 10 min followed by mild reduction in flowing hydrogen at 300°C for 1 hr. For each set of measurements the first oxygen exposure at 25°C was initiated after a 15-min room-temperature evacuation of the sample (vacuum pressure was 10^{-5} Torr). The sample was exposed to 500 Torr oxygen for 45 min before volumetric measurement of the oxygen uptake, $(X_{O_2})_1$. The hydrogen titration was next initiated following a 15-min evacuation. Again according to standard procedure the sample was exposed to approximately 500 Torr hydrogen for 45 min before measurement of the hydrogen uptake X_{H_2}. The second oxygen uptake measurement $(X_{O_2})_2$ was then initiated following 15 min of evacuation. The uptake values in Table 7 were obtained by linear extrapolation to zero pressure. The magnitude of the oxygen uptake after 2½ hr was found to increase by only 3.5% for the 12.1% Pt–Fe/C sample compared to the uptake measured after 45 min of exposure. For the same sample the drift in hydrogen uptake measured over a 10 hr period was only 7% of the total. The ratio of uptakes for both catalysts reduced at 450°C is 3:4:2 compared to 2:2:1 measured for 12.1% Pt–Fe/C following treatment in oxygen at 300°C for 10 min. The former ratio and values of the uptakes can be reproduced by again flowing hydrogen over the sample at 450–500°C and repeating the uptake measurements.

Discussion

Evidence for Small Alloy Particles

For the most part, Pt and Fe appear alloyed together in the supported crystallites. None of the Pt–Fe/C samples exhibited X-ray diffraction patterns corresponding to Pt or Fe metallic phases, or characteristic Mössbauer spectra of metallic iron, or ferromagnetic impurities in excess of 0.2% (*29*).

That the supported metallic particles are very small is indicated by X-ray line broadening, superparamagnetic behavior in Mössbauer spectra and chemisorption measurements. As discussed later, the latter reveal particles between 15 and 30 Å (Table 1). To interpret Mössbauer spectra

TABLE 7

Hydrogen and Oxygen Uptake X (μmole/g) at Room Temperature

Sample	Pretreatment	$(X_{O_2})_1$	X_{H_2}	$(X_{O_2})_2$	Uptake ratios
1% Pt-Fe/C	reduced 8 hr at 490°C	29.3	35.3	17.0	0.83:1.0:0.48
12.1% Pt-Fe/C	reduced 24 hr at 450°C	192	265	132	0.72:1.0:0.50
same	exposed to O_2 at 300°C (10 min) reduced 1 hr at 300°C	217	209	110	1.0 :1.0:0.52

of such small Fe–Pt particles, the simplest assumption is that there are two kinds of iron: bulk iron giving an inner doublet and surface iron with a larger quadrupole splitting characteristic of a lower symmetry giving an outer doublet. When the spectra are decomposed in this way, as typified by Fig. 1, results are obtained which support the view that the samples contain Fe–Pt alloys.

Thus, the isomer shifts of the inner doublet are in excellent agreement with values for corresponding bulk alloys of Pt–Fe (Table 2). The slight decrease of the isomer shift from 0.35 to 0.30 as the iron content in platinum is varied from 1 to 50 atomic% reveals the apparent insensitivity of the IS to the relative number of Fe or Pt nearest neighbors and to particle size even down to 15 Å. Thus the electronic density at the nucleus of Fe^{57} is about the same in a 15 Å particle and in a bulk alloy, suggesting that the overall electronic structure of the metal is not sensitive to particle size, at least above 15 Å.

The values of QS for the inner doublet (Table 4) are seen to change with alloy composition. This variation suggests that the supported alloy particles possess a rather narrow distribution in composition. If this were not the case, the lines for the inner doublet would then be much wider than actually observed (see Fig. 1), as they would be broadened by different QS values corresponding to different Fe contents.

Another argument in favor of alloy formation on carbon supports is that hyperfine splittings, line shapes, and intensities of low-temperature spectra for Pt–Fe/C samples are very similar to those for bulk alloys of corresponding composition (Table 2).

Finally, the Mössbauer spectra of surface iron species, their changes as a result of chemisorption, and chemisorption data themselves can be best understood if Pt and Fe are present together at the surface. These surface effects will now be examined.

Mössbauer Lines of Surface Iron

The observed changes in room temperature Mössbauer spectra following exposure of each reduced alloy catalyst to air and then hydrogen both at 25°C and then to oxygen at 300°C are illustrated in Figs. 3–6 and the corresponding changes in Mössbauer parameters collected in Tables 4 and 5. These changes in IS and QS involve the outer "surface" doublet and in a few instances the inner "bulk" doublet. Changes in IS relate to modifications in the electron density at the Fe^{57} nucleus from which inferences can be made regarding change in electronic structure. Changes in QS reflect changes in the symmetry surrounding the Fe^{57} nucleus.

Further evidence in support of alloying is provided by a change in IS for reduced samples in an atmosphere of H_2 as the Fe content is decreased. Thus for 9.4% Pt–Fe(90/10)/C the outer "surface" doublet is shifted positively with respect to the inner "bulk" doublet by 0.10 mm/sec. This positive IS corresponds to a decrease in electron density at the nucleus of Fe^{57} which appears to be due, in part, by the surrounding Pt atoms with hydrogen adsorbed on them. Indeed, no such effect is found in the bulk as more Pt atoms surround bulk Fe, as discussed above. Also, after evacuation to remove adsorbed hydrogen, the outer doublet disappeared. If then the positive IS due to hydrogen chemisorbed on surrounding Pt atoms in an alloy containing only a small amount of Fe, this effect suggests the possibility of using Fe^{57} as a Mössbauer probe of surface chemisorptive interactions on surrounding atoms that do not exhibit the Mössbauer effect. If confirmed by further work, this phenomenon could be used to study any surface containing a Mössbauer probe.

The increased QS observed after exposure to air at 25°C results from chemisorption of oxygen on the alloy surface and suggests strong chemisorption; in fact, the asymmetry in the electric field apparently extends to nearest and next-nearest neighbors in the bulk as evidenced for 1.0% Pt–Fe(50/50)/C and 1.8 Pt–Fe(66/34)/C by increased QS of the inner doublet corresponding to bulk atoms. Since the alloy particles have average diameters corresponding to about 3 concentric layers of atoms, the nearest and next-nearest-neighbor interactions may involve all internal atoms. The increase in QS of the inner and outer doublets due to oxygen chemisorption at 25°C becomes smaller as the iron content of an alloy decreases indicating again alloy formation in all samples examined. As Fe is surrounded by more Pt neighbors, for 9.4% Pt–Fe(90/10)/C, there is no increase in QS due to room temperature chemisorption of oxygen.

The appearance of a definite Fe^{2+} doublet (see Table 5 and Fig. 3) upon exposure to hydrogen of previously air-exposed samples is evidence that iron-held oxygen at the surface of the alloy is not removed by hydrogen at 25°C but becomes rather an Fe–OH surface complex. Indeed the Mössbauer spectra for the alloys are characteristic of a chemical state intermediate between the fully reduced hydrogen-covered and air-exposed (oxygen-covered) states intimating that platinum atoms on the alloy surface are reduced at 25°C by hydrogen. The appearance of the Fe^{2+} doublet becomes less pronounced as the iron content of the alloy is decreased suggesting that this doublet is a result of hydrogen titration upon oxygen-covered iron sites surrounded by iron whereas the first and fourth peaks correspond to iron surrounded by platinum. Thus in the platinum-rich 9.4% Pt–Fe(90/10)/C sample there was no Fe^{2+} doublet observed following titration with H_2. Again the gradual shift in behavior as the Fe content is varied, is further indication of alloy formation in all cases. It must be noted that the phenomena just discussed form the basis for the Benson–Boudart titration of supported platinum (*16*) and the behavior suggested by the Mössbauer spectra of Fe–Pt alloys will be used now in the discussion of the stoichiometry of the titration of our alloy samples by H_2 and O_2 chemisorption.

Chemisorption of H_2 and O_2 on Pt–Fe Alloys

As suggested by the discussion of Mössbauer spectra of Fe–Pt alloys titrated with H_2, plausible stoichiometries of interaction of surface Pt and Fe with H_2 and O_2 are written as follows. For a reduced sample of Pt–Fe/C exposed to oxygen or air (where x^s = mole fraction of iron at the surface):

$$x^s\text{Fe–H} + (1 - x^s)\text{Pt–H} + 3/4O_2 = x^s\text{Fe–O} + (1 - x^s)\text{Pt–O} + \frac{1}{2}H_2O \quad (1)$$

Upon subsequent titration with hydrogen:

$$x^s\text{Fe–O} + (1 - x^s)\text{Pt–O} + \frac{(3 - 2x^s)}{2}H_2 = x^s\text{Fe–OH} + (1 - x^s)\text{Pt–H} + (1 - x^s)H_2O \quad (2)$$

Upon reexposure to oxygen:

$$x^s\text{Fe–OH} + (1 - x^s)\text{Pt–H} + \frac{(3 - 2x^s)}{4} = x^s\text{Fe–O} + (1 - x^s)\text{Pt–O} + \frac{1}{2}H_2O \quad (3)$$

The ratio of oxygen, hydrogen and oxygen uptakes from Eqs. (1–3) are $3/2(3 - 2x^s)$: 1.00:0.50. Corresponding measured gas-uptake ratios for both 1.0% and 12.1% Pt–Fe(50/50)/C samples reduced at 450°C are shown in Table 7. The measured uptake ratios compare favorably with ratios predicted from Eqs. (1–3) for $x^s = 0.50$ and 0.60. For these values of x^s, the quantity $3/2(3 - 2x^s)$ is equal to 0.750 and 0.833, respectively, as compared to observed values of uptake ratios equal to 0.72 and 0.83 for both samples. If the stoichiometric Eqs. (1–3) represent reasonable approximations, we conclude, tentatively, that the surface composition of the 1.0% and 12.1% Pt–Fe(50/50)/C samples does not differ by more than 10% from the nominal composition before and after exposure to O_2 at 25°C.

If, however, we look at the measured uptakes of oxygen, hydrogen, and again oxygen listed in Table 7 for 12.1% Pt–Fe (50/50)/C following the 10-min treatment in oxygen at 300°C for one hour, a change in stoichiometry has occurred. Indeed the ratio of uptakes following this treatment is 1.0:1.0:0.52. These data suggest that oxygen treatment at 300°C reconstructs the surface. In fact, the uptake ratios according to Eq. (1–3) are now consistent with 75 atomic% iron at the surface ($x^s = 0.75$). The surface has been enriched in iron as a result of the treatment of the sample in O_2 at 300°C.

This treatment at 300°C was used for the determination of platinum dispersion for another reason. The contamination of catalyst surfaces with carbon is an old problem. In the case of carbon-supported platinum, it has been observed that the platinum surface is contaminated with carbon deposits during the reduction process but that oxygen treatment at 300°C for 10 min is adequate to remove the carbon impurities (*30*). Thus values of D_{Pt} were obtained from hydrogen titrations on surfaces that had been treated at 300°C in O_2 for 10 min. The values of D_{Pt} depend on measured uptakes X_{H_2} and surface composition x^s as follows from Eq. (2):

$$D_{\mathrm{Pt}} = \frac{0.0390 X_{\mathrm{H}_2}}{\mathrm{wt\%\ Pt}} \cdot \frac{(1 - x^s)}{(3 - 2x^s)} \qquad (4)$$

This relation will now be used together with values of D_{Fe} obtained directly from Mössbauer spectra to calculate x^s by means of the relation

$$x^s = \frac{xD_{\mathrm{Fe}}}{(1 - x)D_{\mathrm{Pt}} + xD_{\mathrm{Fe}}} = \frac{xD_{\mathrm{Fe}}}{D_T} \qquad (5)$$

which follows directly from the definitions of D_{Fe} and D_{Pt} for alloys of nominal and surface atom fractions of Fe equal to x and x^s, respectively. Let us note here that the relation:

$$D_T = \frac{x}{x^s} D_{\mathrm{Fe}}$$

derived from (5) was used to calculate values of D_T listed in Table 1, with values of D_{Fe} and x^s taken from Table 8. Exceptions are for the samples in Table 1 containing 12.1 and 3.9% metal for which D_T was calculated from Eq. (2) with experimental values of X_{H_2} and the assumption that $x = x^s$.

Surface Composition of Pt–Fe Alloys

The calculation of D_{Fe} from Mössbauer data depends upon (a) the validity of the separation between surface and bulk peaks and (b) knowledge of the relative recoil-free fractions or Mössbauer absorption probabilities for surface and bulk atoms. That the Mössbauer effect for Fe^{57} surface atoms consists of a doublet with broad lines separated by a splitting larger than for bulk atoms has been found for Co^{57} evaporated on tungsten (*31*). In the present study, the separation of the inner bulk doublet from the outer surface doublet by computer fitting was unambiguous for all room-temperature spectra and for even several low temperature spectra. Indeed, the appearance of broad shoulders for the apparent doublet structure in Fig. 6 is visual evidence for the outer surface doublet. The assumption of constant recoil-free fraction for both surface and bulk atoms due to strong chemisorption finds support in the discussion of Mössbauer surface phenomena by Goldanskii and Suzdalev (*10*). Both theoretical calculations and experimental investigations reviewed by these authors indicate that the recoil-free fraction is generally smaller for metal atoms in the surface and significantly smaller for atoms adsorbed on the surface. The model presented indicates that the decrease in absorption probability is related exponentially to the increased mean-squared displacement of the atoms at the surface. The displacement in turn is inversely dependent upon the number of nearest and next-nearest-neighbor bonds. Thus for metal atoms at a clean surface the broken or unsaturated bonds will contribute significantly to increase the mean squared displacement normal to the surface. If, however, chemisorbed species are strongly held by surface metal atoms, the otherwise broken or unsaturated bonds are saturated causing the mean-squared displacement to decrease. Goldanskii and Suzdalev expect the Mössbauer effect probability for chemisorption to be higher than for physical adsorption (*10*). Thus for strong chemisorption of hydrogen or especially oxygen on Pt–Fe/C samples it is reasonable to assume that the Mössbauer absorption probability of surface Fe atoms will be substantially the same as that of bulk atoms. The recoil-free fractions and Debye temperatures in Table 6 are good evidence that this is indeed true for small particles of Pt–Fe/C. If, however, the chemisorbed molecules are removed by evacuation at high temperature the adsorption probability of the outer surface peak is expected to decrease. Indeed the spectrum for 9.4% Pt–Fe(90/10)/C after the evacuation at 560°C was best fitted by only one doublet with parameters characteristic of internal or bulk alloy atoms (Table 4). The apparent decrease in area of the outer surface doublet and decrease in overall spectral area suggest that the cleaned surface has a significantly decreased recoil-free fraction compared to bulk.

Thus, the assumption of equal recoil free fraction for surface and bulk iron provided that the surface is covered with either hydrogen or oxygen appears justified in first approximation. Values of D_{Fe} reported in Table 4 were calculated accordingly from spectral areas.

The values of surface composition x^s recorded in the upper part of Table 8 were calculated by means of Eq. (4 and 5), with experimental values of hydrogen uptake X_{H_2} and D_{Fe}.

To obtain the values of x^s in the lower part of Table 8, it was assumed that the true value of D_T (or particle size) did not change as a result of exposure of the reduced hydrogen-covered surface to oxygen at 25 or 300°C. This was shown to be true within experimental error by the chemisorption measurements discussed in the earlier section, pertaining to the 12.1% Pt–Fe(50/50)/C sample. Thus we calculated values of x^s by means of Eq. (5) with D_{Fe} values from Table 4.

The results of Table 8 appear consistent with the results inferred earlier from chemisorption data and assumed stoichiometries based on Eqs. (1–3). Thus, values of x and x^s differ by less than 10% when alloy samples have been exposed to air at 25°C but significant enrichment in surface iron takes place following exposure of the alloy particles to oxygen at 300°C. Thus results from chemisorption measurements and Mössbauer data lead to similar qualitative and quantitative results. But chemisorption data alone, based alone on surface stoichiometries would have led to very speculative values of surface composition. And Mössbauer data alone could have revealed only values of D_{Fe} without the help of chemisorption data. Thus to determine surface composition of a supported binary alloy, two independent measurements appear necessary, as already indicated earlier by Anderson *et al.* (*2*, *3*).

TABLE 8

Dispersion and Surface Composition of Pt–Fe/C Alloy Catalysts

Total metal wt%	$\%D_T$	$\%D_{\mathrm{Fe}}$	$\%D_{\mathrm{Pt}}$	x	x^s
After exposure to O_2 at 300°C, 10 min					
1.0	62	79	45	0.51	0.65
1.8	61	68	57	0.34	0.38
1.0	64	85	57	0.25	0.33
9.4	40	72	36	0.101	0.182
After exposure of reduced catalyst to air at 25°C					
1.0	62	57	68	0.51	0.47
1.8	61	56	63	0.34	0.31
1.0	64	65	64	0.25	0.25
9.4	40	53	38	0.101	0.135

While the stoichiometric Eqs. (1–3) may be only approximate, it is important to note that different assumptions could be compatible with the chemisorption data but would lead to only minor changes in the calculated values of surface composition. None of the above conclusions would change: surface and bulk composition of small alloy particles appear to be about the same in hydrogen or after exposure to air at 25°C, but enrichment in iron of the surface follows oxidation at 300°C. This last result is only natural if it is remembered that heats of chemisorption of oxygen at −136 and −64 kcal/mole for Fe and Pt, respectively.

Finally we have shown the value of Mössbauer spectroscopy in providing information on surface states during a catalytic event, e.g., the hydrogen–oxygen reaction, even at low concentrations of the Mössbauer isotope which can be considered as a probe of surface events.

Admittedly, we do not pretend to understand or explain all the Mössbauer parameters reported in this paper, especially those of Tables 4 and 5. For instance, it is not clear to us what should be the effects of chemisorbed gases on the direction of chemical shifts. It is hoped that further work will resolve the many questions raised in this work. In particular, it is possible that special constraints imposed to the fitting of our spectra might lead to different results concerning some of the reported Mössbauer parameters. In this paper, we chose, for the sake of simplicity, to impose no constraints on the fitting except in the few cases mentioned. We believe the results obtained on the surface analysis by Mössbauer data are consistent with those obtained from chemisorption so as to justify this simplest approach in the fitting of the spectra, at least for now.

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