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NOTES

Preparation of a Well Dispersed Platinum–Iron Alloy on Carbon

One of the newest and most useful techniques for studying the electronic and chemical behavior of iron catalysts is Mössbauer spectroscopy (*1, 2*). Recently we began investigating the application of ^{57}Fe as a Mössbauer probe in the study of adsorption on platinum catalysts. Thus it became desirable to prepare well-dispersed alloys of platinum with iron. Using a graphitized carbon support, we have succeeded in preparing platinum–iron alloys, having estimated average particle dimensions in the range of 30–40 Å. The method has also been successful for preparing equally well-dispersed platinum catalysts on the same support and is believed to be generally applicable for the preparation of other supported metals and alloys on graphitic carbon.

The catalyst preparation consisted of four consecutive steps. The first step was a partial oxidation of the support, a high purity, nonporous, graphitized channel black known as Graphon with a BET surface area of 87 m^2/g obtained from the Cabot Corporation. This carbon was ground to 48 mesh and burned in a muffle furnace at 600°C until approximately 50% by weight had been burned off by air. The sample was removed from the furnace every 2–3 hr in order to be weighed and stirred. The total time required to burn off about 50% of a 30 g sample was approximately 12 hr.

The second step was impregnation of the preoxidized carbon with a chloroplatinic acid and ferric nitrate solution in a four to one mixture of benzene to ethanol (absolute). The metal concentration was adjusted so as to produce the desired alloy composition and total metal loading. The amount of solvent was fixed by using 50 ml/g of carbon. A mixture of salt solutions and carbon was mechanically shaken while nitrogen was bubbled through the suspension at a flow rate of 200–500 cc/min until the solution evaporated to dryness, i.e., after 40–60 hr for a 10 g sample of catalyst in 500 ml of solution.

The next step consisted of drying the impregnated samples during 12 hr under vacuum at 100–150°C or at 70°C for the samples containing Pt–Fe or Pt alone, respectively. The fourth and last step was a reduction at 500°C in flowing hydrogen gas (20–30 cc/min) at atmospheric pressure for 7–10 hr.

Possible explanations of some details of the preparation are as follows. First, burning of the nonporous carbon particles in air is known to form pits and pores (*3*), covered with oxygenated groups (*4*) which because of their hydrophilicity (*5*), may serve to take up impregnated salts. Besides, the pores created by oxidation may isolate the reduced metal particles preventing their migration and growth during the reduction treatment. Indeed, as previously reported (*6*), the dispersion of platinum on a similar carbon support impregnated in a manner similar to that described above but with the omission of the preburning step is lower by a factor of two than that reported in this note (Table 1).

Second, the use of organic solvents in the impregnation was also reported previously to be more favorable than water as a result of the hydrophobicity of graphitic carbon (*7*).

Although it is common practice to calcine an impregnated sample in air at high temperature (e.g., 500°C) before the reduc-

TABLE 1
PtFe AND Pt CATALYSTS SUPPORTED ON CARBON

Wt % total metal	Relative amount of metals, at. %		% Dispersion of platinum
	Fe	Pt	
3.9% Pt-Fe/C	50	50	35
12.1% Pt-Fe/C	48	52	31
9.4% Pt-Fe/C	10	90	38
1% Pt/C	—	100	52
10% Pt/C	—	100	23

tion step, this procedure may lead to a less well-dispersed metal catalyst in the case of alloy preparations—especially those involving iron. For example, it was observed that heating a carbon sample impregnated with chloroplatinic acid and ferric nitrate at 500°C in air for 6 hr resulted in formation of large crystallites of α-Fe_2O_3 approximately 500 Å in diameter and large platinum crystallites of 100 Å diameter (as determined by X-ray diffraction). For this reason, all samples of Table 1 were reduced directly after mild drying *in vacuo*. It also appears that the presence of platinum changes significantly the dispersion of iron on carbon supports. Indeed, the reduction at 450°C of several carbon samples impregnated with various salts of iron did not yield small particles of iron metal. Rather, X-ray examination of 3% Fe/C powders indicated particle sizes of iron ranging from 200–600 Å in diameter.

The composition and dispersion for three platinum–iron alloy catalysts and for two platinum catalysts are given in Table 1. Dispersion of platinum, i.e., percentage of platinum in each sample which finds itself at the surface, was determined by means of a hydrogen titration of samples preexposed to oxygen at room temperature following the method of Benson and Boudart (*8*).

In the case of the samples containing only platinum, the assumptions made in the calculation of the dispersion were the usual ones which were shown to be correct by X-ray line broadening and electron microscopy of less well-dispersed Pt/C samples (*6*).

In the calculation of dispersion for the Pt–Fe/C samples, four assumptions were made. First, it was assumed that one oxygen atom was removed from each surface platinum atom but not from iron atoms. Second, it was assumed that each oxygen atom associated with a surface iron atom adsorbed one hydrogen atom during the titration. The third assumption is that made normally, namely that each platinum site takes up one hydrogen atom. Finally, it was necessary to assume a surface composition of the alloy particles which was for the present assumed to be the same as the nominal metal composition of the sample.

That these assumptions are not unreasonable is first indicated by the good agreement between values of dispersion for platinum samples with and without iron at comparable metal loadings, as shown in Table 1.

For the 50 at. % iron alloy X-ray diffraction patterns were characteristic of the ordered tetragonal PtFe structure (*9*). The X-ray pattern for the 10 at. % iron alloy indicated *d* values intermediate between those of ordered PtFe and platinum metal. In all cases the X-ray peaks were very broad showing very small particles to be predominant in the sample. Electron micrographs of the 50 at. % iron alloy showed particles in the 30–40 Å range to be present in the sample. This size is in excellent agreement with that corresponding to the dispersion value of Table 1, namely about 30 Å for spherical particles with an average site density corresponding to 8.5 $Å^2$/atom.

From X-ray data and magnetic susceptibility, it appears that Pt and Fe are alloyed on the carbon support and that if either metal exists separately, it represents only a small fraction of the total amount in the alloy phase. This conclusion is strengthened by catalytic data on the decomposition of ammonia—a reaction catalyzed by iron but not by platinum—and on the isomerization of neopentane—a reaction catalyzed by platinum but not by iron (*10*).

In particular, we have found that the turnover number for ammonia decomposition on the 50–50 Pt–Fe/C sample calculated per iron atom with a dispersion of iron identical to that of platinum in line with the fourth assumption listed above, is only about four times smaller than that measured for a supported iron catalyst under identical conditions (*11*).

With neopentane, our data on the same sample are summarized in Table 2 and compared to earlier data obtained under identical conditions on an earlier Pt/C catalyst (*12*). The striking result of Table 2 is that the selectivity for isomerization of neopentane on the Pt–Fe/C sample is identical within experimental error to that found earlier on the Pt/C catalyst. Since iron is quite active for hydrogenation of neopentane but totally inactive for isomerization of that molecule, this finding implies that, if there is any unalloyed iron, it must be present in a very small amount. Besides, iron exposed at the surface of the alloy must be very inactive with respect to neopentane.

Finally, the Mössbauer parameters of the reduced 50–50 Pt–Fe/C sample did not exhibit any detectable lines of metallic iron but were very similar to those reported by Palaith *et al.* (*13*) for Pt–Fe alloys containing between 24 and 36 at. % Fe. Marked changes in these Mössbauer spectra were observed as the reduced samples were exposed to the air first, then to hydrogen, both at room temperature. The possibility of following a platinum titration by Mössbauer spectroscopy again testifies to the high degree of dispersion of the metallic particles and to the existence of the alloy since iron alone cannot be reduced at room temperature by hydrogen. Also, as shall be shown in detail elsewhere, the Mössbauer spectrum of the disperse alloy following a titration is not the same as that before the titration or that of the alloy following a high temperature reduction with hydrogen. This led to the assumption of hydrogen being held on the oxygen associated with the surface iron.

TABLE 2

TURNOVER NUMBERS AND SELECTIVITY FOR NEOPENTANE ISOMERIZATION (N_I) AND HYDROGENOLYSIS (N_H) ON CARBON-SUPPORTED CATALYSTS[a]

Catalyst	$N_I \times 10^3$ sec^{-1}	$N_H \times 10^3$ sec^{-1}	$S = N_I/N_H$
12% Pt–Fe (50/50) C	2.5	1.0	2.5
1% Pt/C	86	34	2.5

[a] Conditions: 370°C; total pressure 1 atm; hydrogen to hydrocarbon ratio 10:1.

While the exact surface composition of the disperse alloys remains to be determined by future more quantitative work, there is little doubt from the above evidence, that we have succeeded in preparing Pt–Fe alloys with a degree of Pt dispersion not far from that shown in Table 1 with amounts of unalloyed iron too small to be detected by magnetic susceptibility, Mössbauer spectroscopy and catalytic activity.

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NMR Studies of Olefin Adsorption on Zinc Oxide

Nuclear magnetic resonance has been used for surface studies of molecular motion, (*1*), orientation (*2*) and chemical interactions (*3*). Because of the inherent insensitivity of NMR most of these studies have been restricted to systems of large surface area, and to coverages greater than a monolayer.

We report here 100 MHz proton resonance studies of several chemisorbed species at a surface area of less than 10 m^2/g with coverages of less than a monolayer.

The adsorption of the light olefins on zinc oxide has been the subject of extensive infrared and kinetic investigations by Connor *et al.* (*4*) Connor and Kokes (*5*) and Dent and Kokes (*6–11*) which provide excellent material for comparison.

The NMR spectra were recorded at 100 MHz utilizing a Varian XL-100 spectrometer, with 12 mm sample tubes, and external lock. The homogeneity of the magnet was trimmed by using a double sample tube with zinc oxide in the outside, and tetramethylsilane (TMS) or dimethyl sulfoxide (DMSO) in a concentric inner tube.

Gases used were Matheson C.P. grade. The zinc oxide was Kadox-25 from the New Jersey Zinc Company, and had a surface area of 9 m^2/g (BET). It was treated as in investigations (*4–11*); evacuated for 2 hr at 450°C, heated in 160 Torr of O_2 at 450° for a further 2 hr with a liquid nitrogen trap in the system, cooled to room temperature, then evacuated again for 1 hr.

Figures 1a and 1b show the NMR spectra of ethane and *n*-butane physically adsorbed on ZnO, which were recorded for purposes of comparison. Figure 2a shows the spectrum of ethylene at a coverage of 1.25×10^{-5} moles/g (approx 0.2 monolayers). Figure 2b shows the spectrum of propene at a coverage of 3.1×10^{-5} moles/g. All of these spectra were recorded at room temperature. The lines are broad, having a full width at half-height of 30 to 120 Hz, presumably due to partially averaged dipole–dipole interaction (line width is not changed by spinning). Spin–spin splitting is not resolved. As shown, however, the resolution is good enough to distinguish CH_3–, –CH_2–, and olefinic protons.

Chemical shifts of the adsorbed species were measured relative to external TMS samples. The values were corrected by —0.7 ppm for the difference in diamagnetic susceptibilities of ZnO and TMS, using the long cylinder aproximation (*12*). The volume susceptibility of ZnO was calculated using the observed bulk density of the powder, and the data of Trew *et al.* (*13*). These results are presented in Table 1, together with the chemical shifts observed by other workers (*14–16*) for the nonadsorbed molecules.

As shown, the physically adsorbed paraffins have no chemical shift relative to the free molecules, within our experimental uncertainty.

In contrast, the adsorbed olefin reso-