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NOTES

Hydrogen Adsorption on Platinum/Silica Catalysts

The hydrogen–oxygen titration method has been used to measure the surface area of platinum on hydrophilic supports such as alumina or silica with the stoichiometry at 25°C given by (*1*)

$$\text{PtO (surface)} + 2H_2\text{ (g)} \rightarrow \text{PtH}_2\text{ (surface)} + H_2O\text{ (support)}$$

Previously, values of 2.9 (*2*) and 3.2 (*3*) were reported for the ratio of net hydrogen titration to net oxygen adsorption on Pt/alumina at 250°C and at room temperature, respectively, corresponding to

$$\text{PtO (surface)} + \tfrac{3}{2}H_2\text{ (g)} \rightarrow \text{PtH (surface)} + H_2O\text{ (support)}$$

The latter assumption of a Pt (surface)/H atom ratio of unity is commonly made and ratios of Pt (total)/H atom approaching unity are cited as evidence for very high dispersion (*4–6*). Crystallite sizes determined by X-ray diffraction and from H_2 adsorption on sintered Pt/alumina catalysts agree (*4*) and provide some direct evidence for the view, observed with bulk platinum catalysts, that each surface platinum atom adsorbs one hydrogen atom.

These H_2 adsorption measurements, mostly on alumina-based catalysts, were usually made at pressures of several hundred torr. The picture seems to be clearer for silica-based platinum catalysts with apparent hydrogen monolayer coverage at pressures of a few torr. Direct observation of the crystallite size has been made (*7*) for a 2.5% Pt/silica impregnation catalyst using X-ray line-broadening and electron microscopy and compared with sizes from H_2 adsorption at 0°C assuming each H atom occupies 11 Å^2. Results are presented here, using a similar approach to measure the Pt (surface)/H atom ratio, for a series of silica impregnation catalysts with a wide range of Pt contents. Previously, it was found that the Pt (surface)/CO ratio varied with crystallite size in these catalysts (*8*). Comparison of the adsorption of H_2 and CO on highly dispersed Pt-on-silica catalysts where physical methods are not applicable, also indicates how hydrogen is adsorbed on very small platinum crystallites.

The procedure used for preparing Pt/silica catalysts by impregnation with chloroplatinic acid has been described (*9*). The catalysts shown in Table 1 were reduced *in situ* at 210°C for 2 hr in a stream of hydrogen at 760 torr (diffused through palladium), and outgassed in vacuum overnight at at 500°C. Platinum/silica high-dispersion catalysts (Table 2) were prepared by the method described in ref. (*10*) where platinum ammine is adsorbed on silica gel. Unless otherwise indicated, these catalysts were prereduced in flowing hydrogen (760 torr) for 2 hr at 20°C, followed by a temperature increase over 2 hr to 300°C and maintained in a hydrogen stream for a further 2 hr.

The method used to extend the X-ray line-broadening technique to provide information on the proportion of platinum in crystallites <50 Å size has been reported (*9*). The original assumption of a mean size of 25 Å for these small crystallites was confirmed by electron microscopy (*8*). For the calculation of the number of exposed platinum atoms from crystallite size measurements, the platinum crystallites were envisaged as regular cubes exposing five faces to the adsorbing gas, and each surface

TABLE 1
Pt(SURFACE)/H RATIOS ON IMPREGNATED Pt/SiO$_2$ CATALYSTS

Pt content (%)	Pt detected by X-ray diffraction: Crystallite size (Å) (111)	(200)	(220)	Fraction detected	Exposed Pt (atoms/g cat) ×10^{-19}	Calc. mean size[a] (Å)	H adsorption (atoms/g cat) ×10^{-19}	Pt (surface) / H atoms
1.06	75	—	—	0.60	0.67	42	0.63	1.06
6.9	55	60	55	0.45	5.47	33	4.01	1.36
8.5	75	70	60	0.83	3.98	56	3.99	1.00
10.0	110	95	95	0.93	3.13	84	2.87	1.09
10.0[b]	105	100	95	0.99	2.58	102	2.26	1.14
11.7	130	120	120	1.00	2.38	130	2.31	1.03
13.3	160	140	130	0.98	2.45	143	1.72	1.42
								Mean 1.16

[a] Calculated from X-ray data.
[b] Reduced at 500°C.

platinum atom was assumed to occupy 8.9 Å^2. Hydrogen or carbon monoxide ("spectrographically pure" gases) were chemisorbed at 25°C using a conventional volumetric apparatus. Typical isotherms, for impregnation catalysts with low and high Pt contents, corrected for dead space and the small adsorption on the silica support are shown in Fig. 1. X-Ray diffraction and X-ray fluorescence analysis for Pt content were made after the adsorption experiments.

Table 1 shows the number of exposed platinum atoms per gram of catalyst calculated from crystallite size measurements compared with the number of hydrogen *atoms* adsorbed. The ratio Pt (surface)/H atoms shows no discernible trend with increasing crystallite size, unlike Pt (surface)/CO ratios measured on similar catalysts (*8*), yielding a mean value of 1.16.

Some of the sources of error may be briefly considered. The crystallites are conveniently treated as cubes since the mean size from X-ray line-broadening is the cube root of the volume whereas some other crystallite shapes require a compensating factor (*8*). The area occupied by a surface platinum atom varies with crystal face and the value obtained from platinum black (*7*), 11 Å^2, yields, in the present work, a mean Pt (surface)/H atom ratio of 0.92.

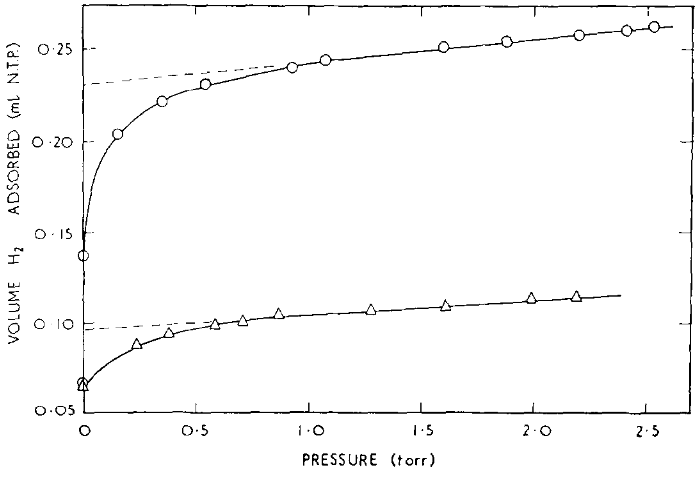

FIG. 1. Corrected hydrogen adsorption isotherms at 25°C for Pt/silica catalysts: ○, 0.535 g 11.7% Pt catalyst. △, 0.820 g 1.06% Pt catalyst.

TABLE 2
H ATOM/CO RATIOS ON HIGH-DISPERSION Pt/SiO_2 CATALYSTS

Pt content (%)	CO adsorbed (ml/g cat)	H_2 adsorbed (ml/g cat)	Mean crystallite[a] size (Å)	H atom / CO
2.45	1.589	0.879	13	1.11
3.12[b]	1.019	0.592	(27)	1.16
3.12[c]	1.682	0.880	16	1.05
3.75	2.283	1.277	14	1.12
3.78	2.216	1.267	15	1.14
4.45	2.441	1.474	16	1.21

[a] Calculated from CO adsorption data.

[b] Prereduced at 80°C for 2 hr, reduction probably incomplete.

[c] Prereduced at 210°C for 2 hr.

Small errors in determining the weight of catalyst used in the adsorption measurements arise from the hydrophilic nature of the silica and the indeterminate chlorine content before reduction. Therefore there is no reason to believe that the Pt (surface)/H atom ratio departs from unity in these catalysts when hydrogen adsorption measurements are made at low pressures and 25°C.

Under these conditions, the isotherms (see Fig. 1) gave a clear indication of the apparent hydrogen monolayer volume. It was found previously (*11*) that hydrogen adsorption on highly dispersed Pt/silica catalysts at −196°C was practically nonactivated and yielded Pt (total)/H atom-ratios of unity. Raising the temperature to −78°C caused an additional but rather variable hydrogen sorption. However, the total adsorption at 20°C was only slightly greater than adsorption at −196°C and the higher temperature should lead to rapid equilibration and was preferred in the present work.

Table 2 shows the volumes of carbon monoxide and hydrogen adsorbed on highly dispersed Pt/silica catalysts, prereduced as described above, except as indicated. The first three catalysts in the table had been used in a test of benzene hydrogenation activity. All catalysts were again reduced *in situ* at 80°C for 30 min and outgassed at 350°C for 3-4 hr in vacuum before CO adsorption. Before hydrogen adsorption, CO was removed by outgassing overnight at the same temperature.

The H atom/CO ratio is approximately constant with a mean value of 1.13. The errors mentioned above should not be involved in these results. It was found previously that the infrared evidence for 15% bridge-bonding on Pt/silica (*12*), i.e., Pt (surface)/CO ratio = 1.15, leads to close agreement between metal areas calculated from X-ray diffraction and from CO adsorption measurements (*8*, *9*), *providing the crystallites are small.* This ratio might reasonably be expected to apply also to the highly dispersed catalysts shown in Table 2. Hence the Pt (surface)/H atom ratio is given by 1.15/1.13 = 1.02 supporting the observation, from direct measurement, of the ratio reported above.

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