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Hydrogen Chemisorption on Platinum Catalysts

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Hydrogen chemisorption on Pt and Pd, supported on active carbon and alumina, was determined by a rapid desorption technique. Desorption was effected by increasing the sample temperature from 21 to 370°C in less than 1 min. The desorbed hydrogen, swept into a nitrogen carrier gas, was measured from the peak recorded by a chromatographic-type detector. Repetitive determinations on the same sample were consistent within ±3%. The chemisorption data indicated that the dispersion of Pt on active carbon was 47, 32, and 23% for 0.5, 1.0, and 10% Pt–C, respectively. Evidence of carbon monoxide disproportionation on Pt at 370°C and of hydrogen spillover from Pt to active carbon support at 370°C was found.

INTRODUCTION

Supported noble metal catalysts are used widely in the chemical industry. A rapid method for determining metal surface area of these catalysts is desirable in order to compare catalyst activities on a basis of equivalent metal surface area. The purpose of work reported here was to develop such a method using hydrogen chemisorption and to determine the noble metal surface areas of several commercial catalysts. The chemisorption results can also be used to determine noble metal dispersion; i.e., the percentage of total metal atoms exposed as surface atoms.

EXPERIMENTAL METHOD

The apparatus used for the chemisorption measurements is shown in Fig. 1. A Perkin–Elmer–Shell Sorptometer (normally used for physical adsorption measurements) was modified to facilitate hydrogen chemisorption and desorption from the catalyst sample. All of the catalysts tested were prereduced and dried by the manufacturer.

Chemisorption was effected at 21°C by passing a mixture of hydrogen and nitrogen* over the sample. A molten lead bath at 375°C was raised over the sample tube to effect a very rapid heatup and desorption. Nitrogen was used as the carrier gas to give high detector sensitivity for hydrogen. The nitrogen was fed over the sample continuously at 26 cm^3/min and at atmospheric pressure.

The experimental procedure consisted of (1) degassing the 1–4 g catalyst sample in nitrogen to 370°C for 3–5 min; (2) adsorbing hydrogen at 21°C for 2 min; (3) purging with nitrogen at 21°C for 2–5 min to remove physisorbed hydrogen; and then (4) heating to 370°C for 3–5 min to desorb the chemically bonded hydrogen. The chemidesorbed hydrogen was detected in nitrogen carrier gas by a hot wire filament and measured from peak area. The adsorption–desorption steps, two through four, were repeated at least five times, and generally after the first two or three repeats, the desorption-peak areas were constant (within ±3%). Reproducibility of measurements on different samples from the same catalyst lot was ±5%. Oxygen chemisorbed on the noble metal was removed as water during initial desorptions.

This desorption-peak method is similar to that described by Komers, Amenomiya, and Cvetanovic (*1*), although they used temperature programming for sample heatup rather than a step temperature change.

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* Airco hydrogen, prepurified grade, 99.95% minimum. Linde nitrogen, liquidified, 99.997% minimum.

TABLE 1

H_2 AND CO CHEMISORPTION ON SUPPORTED Pt AND Pd CATALYSTS[a]

Catalyst	Chemisorption (cm^3/g catalyst) H_2	CO, expected[b]	CO, measured
0.5% Pt-C	0.15	—	—
1% Pt-C	0.20	0.40	0.7 → 0.3
5% Pt-C	0.96	1.92	1.8
10% Pt-C	1.43	2.86	3.0
0.6% Pt-porous Al_2O_3	0.25	—	—
0.5% Pt-nonporous Al_2O_3	0.054	0.108	0.11
5% Pd-C	0.65	1.30	1.1

[a] All catalysts manufactured by Engelhard Industries. Gas volumes are at ambient conditions, 21°C and 1 atm.

[b] For agreement with the H_2 chemisorption.

DISCUSSION OF RESULTS

The measured volumes of hydrogen chemisorbed on various commercial catalysts are listed in Table 1. These results were the basis for the calculated metal surface areas and dispersions in Table 2. Carbon monoxide chemisorption measurements (Table 1) were also obtained using a similar procedure, but they were not as reproducible as the hydrogen measurements.

For 0.5% platinum on active carbon (0.5% Pt-C) catalyst, the volume of chemisorbed H_2 was 0.15 cm^3 (21°C, 1 atm)/g of catalyst, corresponding to 0.47 g-mole H/g-mole of total Pt. The Pt dispersion is then 47%, assuming one atom of hydrogen is chemisorbed on one exposed Pt atom. The dispersions of Pt on 1, 5, and 10% Pt-C were 32, 31, and 23%, respectively. Total Pt surface area of 10% Pt-C was thus 10 times that of 0.5% Pt-C, a factor which is significantly less than the Pt weight ratio of 20.

The hydrogen chemisorption on two alumina-supported Pt catalysts was also determined. A commercial reforming catalyst, 0.6% Pt on porous alumina, had a higher dispersion (68%) than any of the Pt-C catalysts. A special catalyst with

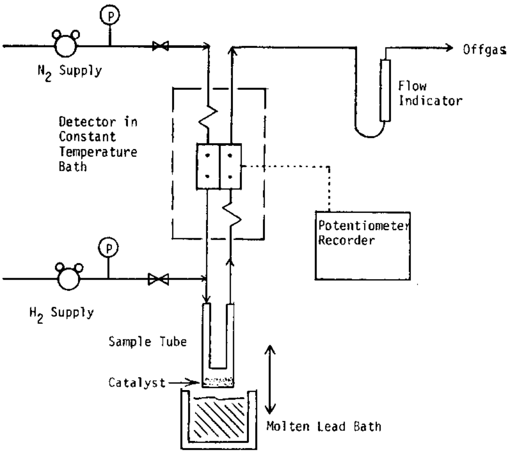

FIG. 1. Hydrogen chemisorption apparatus.

TABLE 2

SURFACE AREA AND DISPERSION OF NOBLE METAL ON SUPPORTED Pt AND Pd CATALYSTS

Catalyst	Metal surface area[a] (m^2/g catalyst)	Metal dispersion[b] (%)
0.5% Pt-C	0.66	47
1% Pt-C	0.88	32
5% Pt-C	4.2	31
10% Pt-C	6.3	23
0.6% Pt-porous Al_2O_3	1.1	68
0.5% Pt-nonporous Al_2O_3	0.24	18
5% Pd-C	—	12

[a] The Pt surface area is calculated assuming 4.4 m^2/ambient cm^3 H_2 chemisorbed or 1.12×10^{15} sites/cm^2 surface area (*4*).

[b] The metal dispersion (percentage of total metal atoms exposed) is calculated assuming one atom of hydrogen chemisorbs on one exposed metal atom.

0.5% Pt on fine *nonporous* alumina had poorer Pt dispersion than the reforming catalyst. However, this catalyst could be useful to obtain specific Pt activity in reactions where pore diffusion affects the activity of a commercial reforming catalyst.

A 5% Pd–C catalyst was found to chemisorb less hydrogen than 5% Pt–C even though the former contains more gram-moles of metal per gram of catalyst. The dispersion of noble metal on 5% Pd–C was 12%, which was lower than that on any of the Pt catalysts. It was noted that hydrogen dissolved in Pd during the adsorption at 21°C, but it could be removed before chemidesorption by adequate N_2 purging at 21°C.

Appropriate control runs were made to check the method. The carbon support alone gave no peak following the same procedure used for catalyst. In addition, a catalyst sample exposed only to the N_2 carrier gas gave no peak when brought up to the desorption temperature. The hydrogen desorption peaks obtained at 370 and 430°C had consistent areas ($\pm 3\%$). The peaks were nearly symmetrical with negligible tailing.

Thermal sintering of Pt on the catalysts was not a problem at the temperature (370°) and time (3–5 min) required for desorption. Hydrogen chemisorption and, thus, metal surface area on a sample of 1% Pt–C was unchanged for a 1-hr sintering test at 430°C in a N_2 atmosphere.

When carbon monoxide chemisorption was attempted, the measurements were not as consistent as those with hydrogen, particularly in the case of 1% Pt–C. Repetitive CO sorptions and desorptions gave successively smaller peak areas, and the desorbed CO was found to be contaminated with CO_2. To agree with the hydrogen result for 1% Pt–C, the CO chemisorption should have been 0.4 cm^3/g catalyst. The measured CO chemisorption, however, was 0.7 cm^3/g after three desorptions and 0.3 cm^3/g after nine desorptions. The initial high results could be due to CO interaction with oxygen on the support. Subsequent low results could be due to coking of the noble metal surface, which is discussed below. All of the catalysts tested showed this trend with repetitive CO chemisorption, but the effect was not as pronounced as that for 1% Pt–C. The values listed in Table 1 are the average results for the third, fourth, and fifth CO sorption–desorptions. Agreement between the CO and H_2 results for catalysts other than 1% Pt–C was generally within 10%.

As noted above, there was an indication of metal surface area loss during repetitive CO measurements. Further experiments showed that prolonged catalyst exposure to CO at 370–430°C caused a significant decrease of metal surface area. For example, when the 0.6% Pt–Al_2O_3 reforming catalyst was exposed to pure CO for 1 hr at 430°C, the H_2 chemisorption decreased from 0.25 to 0.03 cm^3/g catalyst. Oxygen and hydrogen treatments (regenerations) partially restored this loss of metal surface area. Carbon dioxide was detected in the offgas during the CO exposure and also during the O_2 regeneration. The Pt surface area of 1% Pt–C catalyst was reduced 40% by a 1-hr exposure to pure CO at 370°C. All of this evidence indicated that metal sites can be covered by carbon from CO disproportionation, $2CO \rightarrow C + CO_2$. Boudart (*2*) has proposed that CO can disproportinate at 600–800°C on spheron-6 supported platinum.

A test was also made to determine the effect on prolonged catalyst exposure to hydrogen. The 1% Pt–C catalyst was treated with hydrogen at 370°C for 5–60 min. After the sample was cooled in hydrogen and purged with nitrogen, the desorption step produced an extremely large peak, 1–2 cm^3 H_2/g in excess of the expected amount chemisorbed on the Pt surface. This extra H_2 chemisorption did not occur on Pt–Al_2O_3 at 370°C and not on active carbon alone. Migration of the hydrogen from Pt atoms to adjacent carbon atoms, or spillover (*3*) at 370°C is a possible explanation. This hydrogen chemisorbed on carbon evolved slowly into the nitrogen carrier gas at 370°C and appeared as a large broad peak.

CONCLUSIONS

1. A hydrogen chemisorption method has been developed for determining

the dispersion of supported noble metals. The method is particularly well suited for rapid evaluation of catalysts used industrially.

2. The dispersion of Pt on commercial Pt–C catalysts decreases as the Pt loading increases.
3. Coverage of Pt surface by carbon (coking) may result from CO disproportionation at 370°C. Rapid catalyst aging is probable under such conditions.
4. Transfer or spillover of hydrogen from Pt to C atoms on Pt–C catalysts appears to occur on prolonged catalyst exposure to hydrogen at 370°C.

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REFERENCES

1. KOMERS, R., AMENOMIYA, Y., AND CVETANOVIC, R. J., *J. Catal.* **15**, 293–300 (1969).
2. BOUDART, M., ALDAG, A. W., AND VANNICE, M. A., *J. Catal.* **18**, 46–51 (1970).
3. BOUDART, M., *Advan. Catal. Relat. Subj.* **20**, 153–166 (1969).
4. SPENADEL, L., AND BOUDART, M., *J. Phys. Chem.* **64**, 204–207 (1959).