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NOTES

Factors Influencing the Determination of Metal Dispersion on Supported Platinum Catalysts by the Gas Chromatographic Pulse Technique

The gas chromatographic (GC) pulse technique for chemisorption of gases on supported metal catalysts has the advantage of rapid determination of metal surface area and dispersion without compromising on accuracy. The method was used for hydrogen and oxygen chemisorption on nickel and platinum catalysts (*1*, *2*) and rhenium catalysts (*3*, *4*) for metal dispersion studies. Freel (*5*) used it for gas titration of platinum surfaces and Menon *et al.* (*6*) for separate determination of platinum and rhenium surfaces in a composite Pt–Re–Al_2O_3 bimetallic reforming catalyst. This is an adaptation of the Benson–Boudart volumetric surface titration (*7*) to the quicker GC technique.

In the above pulse studies the relationship between the amount of catalyst and the volume of the gas pulse is considered somewhat arbitrary (*5*). It would generally be assumed to be sufficient if the pulse volume chosen is within the range of linear response of the detector. Then the amount of catalyst to be taken and the pulse volume could be arbitrarily chosen such that, for the sake of minimizing experimental error, at least a few pulses would be required to fully saturate the catalyst sample. However, we have found that choice of the amount of catalyst and of the pulse volume on a purely arbitrary basis can lead to very erroneous results. Hence a detailed investigation has been carried out to see the effect of carrier gas flow, amount of catalyst and pulse volume on the hydrogen chemisorption measurement. The results obtained are presented here.

The principle of the GC pulse method involves the chemisorption of a gas, say oxygen, on the metal surface and then known amounts of hydrogen are passed over the catalysts in the form of pulses. The hydrogen first reacts with the chemisorbed oxygen and then becomes itself chemisorbed on the metal. For all practical purposes the stoichiometry is taken as follows:

$$\mathrm{Pt{-}{-}{-}O} + \tfrac{3}{2}\mathrm{H_2} \rightarrow \mathrm{Pt{-}{-}{-}H} + \mathrm{H_2O}.$$

This involves three atoms of hydrogen for every exposed platinum atom. Using a gas pulsing valve and the thermal conductivity detector of the GC the total amount of hydrogen consumed in the titration is determined. Knowing the amount of hydrogen chemisorbed on the platinum surface (one-third the titer value) it is possible to calculate the metal surface area, dispersion and average crystallite size. The reverse titration can also be done. The reliability and accuracy of this method have already been shown earlier (*5*, *6*).

A typical determination with a Pt–Al_2O_3 catalyst may be as follows: About 2 g of the dried catalyst is taken in a reactor (1 cm i.d.). Hydrogen is allowed to flow through the bed while the catalyst is slowly heated to 500°C. After reduction of the catalyst for about 1 hr at this temperature, the

TABLE 1

Hydrogen Chemisorption on 0.6% Pt–Al_2O_3 (CK-306)[a] during Increasing O_2–H_2 Titration Cycles[b]

Cycle No.	H_2 chemisorbed (ml, STP/g)	Degree of Pt dispersion
1	0.156	0.45
2	0.182	0.53
3	0.236	0.68
4	0.254	0.74
5	0.256	0.74
6	0.276	0.80
7	0.284	0.82
8	0.281	0.81

[a] Hydrogen chemisorption on this catalyst as determined by the conventional volumetric method was reported (*6*) to be 0.282 ml (STP)/g.

[b] Catalyst amount taken = 2.0 g; gas pulse volume = 0.238 ml (STP); and carrier gas flow rate = 40 ml (STP) min.

catalyst is cooled to room temperature in flowing hydrogen. The system is then purged with the carrier gas, say helium or oxygen-free nitrogen. With the help of a 6-way gas-sampling valve, pulses of air or oxygen are sent through the catalyst to oxidize fully the catalyst surface. Hydrogen pulsing is then started and continued until the hydrogen peaks on the recorder are identical, thus indicating that all the chemisorbed oxygen has been removed and no more hydrogen can be irreversibly chemisorbed on the metal sites. Knowing the gas volume per pulse the amount of chemisorbed hydrogen can be calculated.

Loops of different volumes were prepared and calibrated by filling with mercury. The detector response versus pulse volume (loop volume plus dead volume of sampling valve) gave a good linear relationship in the range studied here (GC unit: Perkin-Elmer Model 900). Hydrogen chemisorption measurements were made on a sample of 0.6% Pt–Al_2O_3 catalyst (Cyanamid-Ketjen CK-306 reforming catalyst) at different conditions. The data obtained are given in Tables 1 and 2 and Fig. 1.

In our experiments it was observed that during the titration of a Pt- - -O surface at room temperature, hydrogen uptake by the catalyst increased with each oxygen–hydrogen cycle until a few such cycles and thereafter became constant. Such an observation was reported earlier by Menon *et al.* (*6*) when using the GC pulse technique

TABLE 2

Hydrogen Chemisorption on 0.6% Pt–Al_2O_3 (CK-306) under Different Conditions

Expt No.	Study	Catalyst amount (g)	Carrier gas flow (ml, STP/min)	Pulse vol (ml, STP)	H_2 chemisorbed (ml, STP/g)	Degree of Pt dispersion
1	Effect of carrier gas flow	1.0	18	0.155	0.266	0.77
		1.0	36	0.155	0.262	0.76
		1.0	64	0.155	0.260	0.75
2	Effect of catalyst amount	0.5	36	0.155	0.222	0.64
		1.0	36	0.155	0.262	0.76
		2.0	36	0.155	0.327	0.95
		3.0	36	0.155	0.320	0.93
3	Effect of pulse volume	1.0	36	0.155	0.262	0.76
		1.0	36	0.238	0.215	0.62
		1.0	36	0.322	0.195	0.56
		1.0	36	0.356	0.183	0.53
		1.0	36	0.528	0.153	0.44
		1.0	36	0.804	0.112	0.32

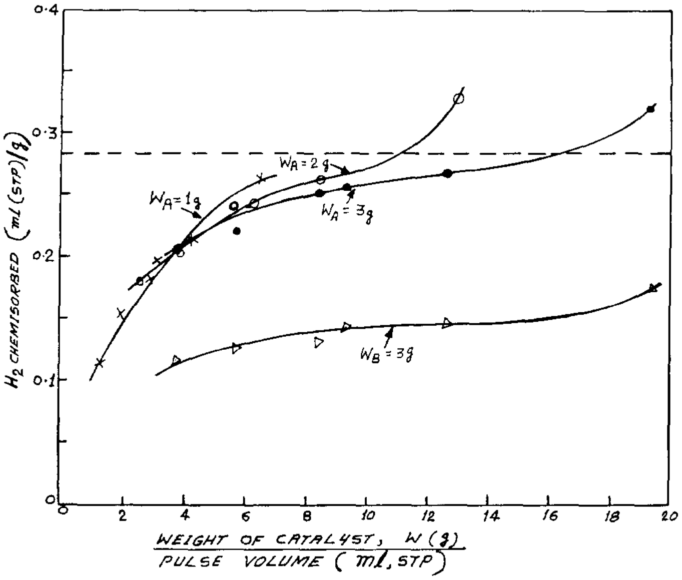

FIG. 1. Dependence of H_2 chemisorption on amount of catalyst and pulse volume. W_A and W_B represent weights of catalyst *A* (CK-306) and B, respectively.

and by Kikuchi *et al.* (*8*) when using *both* the conventional volumetric system and the GC method. Kikuchi *et al.* (*8*) carried out an interesting investigation in order to explain this phenomenon and suggested that the water formed during the titration cycles may be the cause. This observation therefore is not peculiar to the geometry of the apparatus used in our studies. The important point to be noted here is that when metal surface area and dispersion are determined by this method, there may be a tendency to stop with the first titration cycle. The hydrogen uptake value thus obtained could lead to low results of metal surface area/dispersion, as seen in Table 1. The data in Table 1 represent a sample titration. Repeated experiments generated similar data with some scattering of points but the trend was essentially the same as was also reported by Kikuchi *et al.* (*8*). The data in Table 1 thus show that it is necessary that the O_2–H_2 titration cycles should be continued until a constant hydrogen uptake value is obtained. All the results in Table 2 were generated in this manner.

Table 2 shows that the flow rate of the carrier gas has no influence on the chemisorption measurement within the range studied. The amount of catalyst and change in gas pulse volume, however, considerably influence the extent of chemisorption. The amount of hydrogen chemisorbed on this catalyst at room temperature and determined by the standard volumetric method was reported to be 0.282 ml (STP)/g (*6*). The value nearest to this (Table 2) is 0.266 ml (STP)/g which is well within the range of permissible error of estimation. [Repeated determinations yielded values in the range 0.262 to 0.284 ml (STP)/g]. However, scrutiny of the data in Table 2 clearly indicates that an arbitrary choice of conditions for measurement can lead to erroneous results and conclusions.

Figure 1 contains results obtained on the amounts of hydrogen chemisorbed using different quantities of catalyst and pulse volumes. The measurements were made on CK-306 (catalyst A in Fig. 1) and on another commercial catalyst of lower metal dispersion (catalyst B). Both catalyst contain 0.6% Pt on alumina. The broken horizontal line in the figure corresponds to 0.282 ml H_2(STP)/g determined by the standard volumetric method (*6*) for catalyst A. To obtain chemisorption values determined by the GC technique, comparable to that from the standard volumetric method, the measurement should best be done under conditions described by the flat part of the curves. These conditions hold good irrespective of the maximum amount of hydrogen that can be chemisorbed which depends on metal content and dispersion as seen from curves representing catalysts A and B. Hence, for practical purposes the measurement of chemisorption of a gas by the GC pulsing technique on Pt–Al_2O_3 is reliable if the amount of catalyst taken is 2 to 3 g, pulse volume is 0.2 to 0.3 ml (STP), and carrier gas flow rate is 20 to 60 ml (STP)/min. The extent of influence of pulse volume on gas chemisorption tends to decrease with increase in catalyst amount and decrease in maximum amount of gas that can be chemisorbed.

A noteworthy point from Fig. 1 is the tendency of the curves to rise after the "plateau" for which we have no explanation at present.

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