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Comparison of Hydrogen–Oxygen Titration with Hydrogen–Alkene Titration for the Measurement of Platinum Surface Area in Supported Catalysts

The dispersion and surface area of a supported metal is usually measured by the chemisorption of oxygen (*1*), hydrogen (*2*) or CO (*3*) and especially by H_2–O_2 titration (*4–6*). Recently Bond and Sermon (*7*, *8*) disclosed a further new method, namely alkene titration. According to their procedure, hydrogen chemisorbed on the catalyst is picked up by pentene flowing through the reactor and the total amount of pentane evolved is measured by gas chromatography. The method is quite simple and inexpensive. It is likely to be applicable to spent catalysts, after fouling or poisoning. Moreover, it is claimed that one may detect separately hydrogen held by the support as a result of spillover.

It is necessary to assess further whether alkene titration is of general applicability and whether the results agree in general with the widely accepted H_2–O_2 titration. In this paper we describe a part of a systematic comparison of the two methods for platinum catalysts and we conclude that the results of alkene titration give the better correlation with catalytic activity.

The catalysts (2% Pt) have been prepared by impregnating alumina with H_2PtCl_6 solution, drying and reducing in a flow of hydrogen at 500°C, unless otherwise indicated. A variety of aluminas were used, differing by their BET areas and by their SO_4^{2-} content, as given in Table 1. It has already been shown (*9*) that during the reduction of the catalysts at 400°C and above, SO_4^{2-} is gradually reduced to sulfur and the catalytic activity and selectivity are altered. Such catalysts will be called "poisoned" catalysts as opposed to "clean" catalysts.

The H_2–O_2 titrations have been performed at room temperature in a thermobalance after reduction and outgassing at 500°C. The increase in weight of the sample during the titration of chemisorbed hydrogen by oxygen has been used to calculate the metallic area.

Alkene titration has been performed according to the procedure described by Bond and Sermon (*7*) except for the fact that ethylene was substituted for pentene. After the catalyst was given the initial treatment, including reduction at the quoted temperatures, it was cooled down to 100°C under hydrogen and then under nitrogen for 1 h. It was then contacted with a flow of ethylene (0.01 to about 0.1%) in nitrogen and the composition of the effluent gas was monitored by gas chromatography.

A typical result is shown in Fig. 1. As already pointed out by Sermon and Bond (*8*), during the first period alkene reacts with the chemisorbed hydrogen and alkane is the sole product detected. Then the proportion of ethane decreases sharply and the flow of ethylene is gradually restored. Bond and Sermon regarded the final low flow of saturated hydrocarbon as related to slow reverse spillover. Hence, this will be ignored here and the amount of chemisorbed hydrogen will be calculated from the hatched area. It is of interest to note that the steady flow of ethane $F_{C_2H_6}$ is

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TABLE 1

Platinum Surface Areas and Turnover Numbers for Pt/Al_2O_3 Catalysts

Catalysts S content and BET area of the support	Metallic area (m^2/g) after		R	Turnover number (hr^{-1}) for benzene hydrogenation, calcd from	
	Oxygen titration	Alkene titration		Oxygen titration	Alkene titration
A_1[a] (clean) (24 m^2/g)	90	89	1.70	269	271
A_2[a] (clean) (120 m^2/g)	173	180	1.70	285	274
A_3[a] (clean) (180 m^2/g)	140–143	148	1.65	290–285	274
A_4[a] (clean) (290 m^2/g)	130–127	134–121	1.65	268–274	263–290
B_1 (1380 ppm) (180 m^2/g) reduced at 300°C	193–199	205–198	1.65-1.73	306–296	290–296
B_1 reduced at 400°C	166	145	1.85	242	279
B_1 reduced at 500°C	150–164	32.5	2.47	66–61	306
B_1 reduced at 500°C after O_2 titration		33.5	2.63		
B_2[a] (S poisoned) (60 m^2/g) (percents unknown)	134	73	1.83	150	279
B_3[a] (340 ppm) (330 m^2/g)	136–160	91	1.73	196–167	290

[a] These catalysts were reduced at 500°C.

always lower than the incoming flow of ethylene F_0 as finally measured. This point is discussed below.

Table 1 gives the results obtained with a variety of "clean" and "sulfur poisoned" catalysts, including the catalytic activity in benzene hydrogenation. In fact, we have reported the turnover numbers for benzene deuteration ($T = 85°C$, $p_{D_2} = 0.77$ atm, $p_{C_6H_6} = 0.23$ atm), a reaction routinely performed in our laboratory (*9, 10*).

It can be clearly seen that, provided platinum is not poisoned by sulfur (samples A_1 to A_4 and the first B_1), the two methods are in excellent agreement since they give the same areas. Furthermore, the turnover

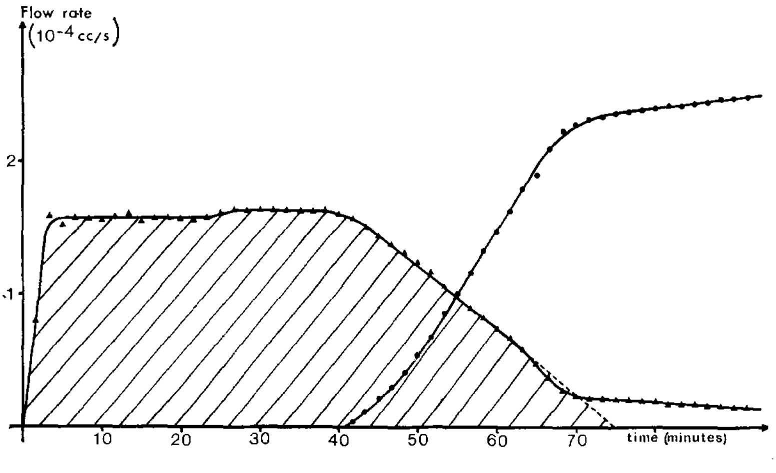

FIG. 1. Ethane (▲) and ethylene (●) flow rates issuing from the catalyst vs time in an alkene titration experiment: 1 g of A_4, $T = 100°C$.

number is constant, as expected, whichever support is used.

For "sulfur poisoned" catalysts, this is no longer true, and the results of H_2–O_2 titration are significantly higher than that of alkene titration. The areas measured by alkene titration are best related to the hydrogenation activity, as evidenced by the turnover numbers. The latter are fairly constant and equal to that of clean catalysts when calculated from alkene titration, whereas they exhibit important variations if H_2–O_2 titration is considered.

Hence H_2–O_2 titration does not measure exactly the metallic area of sulfur poisoned catalysts. This might be a consequence of a possible cleaning of the catalyst by outgassing (10^{-6} Torr, 500°C) or even by the oxygen titration itself. However, this explanation is ruled out by the result of the alkene titration performed on a sample of catalyst B_1 after H_2–O_2 titration (see Table 1). The result is almost the same as that obtained on the preceding sample, proving that the whole process of H_2–O_2 titration did not alter the catalyst.

We are thus led to suppose that during the oxygen titration measurements, some oxygen can be adsorbed on "sulfur poisoned" platinum atoms or on sulfur spread over the platinum. This idea is supported by the measurement of direct oxygen chemisorption on "sulfur poisoned" catalysts, after they have been reduced and outgassed, since the area covered by oxygen atoms is larger than the metallic area as measured by alkene titration or catalytic activity.

Considering now alkene titration in further detail, it is worth noting that the value of $R = F_0/F_{C_2H_6}$ is around 1.7 with unpoisoned catalysts. This can be accounted for by the following equation:

$$5C_2H_4 + 6H_{ads} \rightarrow 3C_2H_6 + 2C_2H_{4_{ads}}.$$

Hence, ethylene adsorbed on the metal would need an average of about 3 platinum atoms, probably as a result of steric hindrance to a close packing (*11*).

The value of R is higher than 1.7 with poisoned catalysts. This can be explained by assuming that ethylene is likely to be adsorbed on some poisoned platinum atoms, which, as already seen, are unable to hydrogenate it. This extra adsorption would lower the outgoing flow of ethane relative to that resulting from the above reaction on the free surface. This hypothesis is corroborated by the fact that the more severe the poisoning, the greater is the departure from the value of $R = 1.7$.

In conclusion, the method of measurement of metallic area of platinum catalysts by alkene titration of chemisorbed hydrogen gives the same results as H_2–O_2 titration with clean catalysts but not with poisoned ones. Indeed, alkene titration measures the free surface of platinum only, as evidenced by the calculation of a constant turnover number in benzene hydrogenation, whatever the extent of catalyst poisoning.

Thus alkene titration appears to be more general than the usual H_2–O_2 titration.

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