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Hydrogen–Oxygen Titration of Surface Platinum in Poisoning Studies

Benson and Boudart proposed the use of room-temperature titration of a surface layer of oxygen by hydrogen to measure the platinum metal area of supported catalysts (*1*). The advantages of this technique were increased sensitivity and minimal interference by the large support surface. Stoichiometries different from that advanced by Benson and Boudart have been proposed (*2*, *3*), and the work of Wilson and Hall indicates that there is a change in oxygen–platinum stoichiometry at room temperature (*3*). The stoichiometry assumed by Benson and Boudart, $Pt_{(s)}O$, applies for large platinum particles (>20–30 Å); and the stoichiometry $Pt_{(s)2}O$ prevails on smaller particles.

In spite of this complication which makes the determination of the absolute number of exposed platinum atoms difficult under certain circumstances, the titration is a useful tool for measuring changes in accessible metal surface upon exposure of the platinum catalyst to various temperatures and environments. Further, it has an inherent advantage over conventional adsorption methods because it dispenses with stringent pretreatment procedures. This is important when studying poisoning of reactions by substances covering and interacting with the platinum surface. Catalyst pretreatment required for adsorption measurements usually differ from the conditions under which a particular poison was deposited and may spread or remove the poison from the platinum surface.

In the evaluation of platinum surface areas of deliberately poisoned monolithic catalysts, the hydrogen uptake during titration was measured using a flow system as described by Weidenbach and Furst (*4*) and Gruber (*5*). Argon carrier gas was passed through the reference side of a thermal conductivity detector, a gas injection valve, the catalyst sample, and back through the detector. The injected volume of hydrogen could be varied from 0.1 to 3 cc. A catalyst sample, after exposure to air, was purged with argon and a slug of hydrogen was injected. Comparison of the peak due to the hydrogen not adsorbed with an identical dose injected over a sample without platinum gave the hydrogen uptake. Comparison of results obtained in this manner with those obtained by titration and hydrogen chemisorption in a conventional static system gave excellent agreement.

The catalyst tested was 0.35% Pt supported on a cordierite honeycomb that contained 10% by weight of a high-surface-area γ-alumina washcoat. Zinc or phosphorus was deposited onto the surface by placing the required amount of poison and a 10-g section of the catalyst in an evacuated and sealed quartz ampoule. The poison was evaporated onto the honeycomb using a flame, and the ampoule was heated in a furnace for 5 hr at 700°C.

Table 1 gives a few examples of platinum

TABLE 1
TITRATION OF ZINC-POISONED SAMPLES

Treatment	H_2 uptake (μmoles H_2/g)
1. Fresh	3
2.5% (w/w) zinc added	0.69
H_2 at 400°C, 1 hr	0.038
O_2 at 300°C, 1 hr	0.24
2. Fresh	3
2.5% (w/w) zinc added	0.50
O_2 at 300°C, 1 hr	0.83
H_2 at 400°C, 1 hr	0.13
O_2 at 300°C, 1 hr	0.16

surface areas for zinc-poisoned catalysts. When initially evaporated onto the sample, the zinc covers a large fraction of the platinum surface. However, treatment in hydrogen further reduces the accessible platinum surface to approximately 1% of its initial value. Upon treatment in oxygen at 300°C, the platinum surface is partially regained. The data pertaining to Sample 2 show that if an oxidative treatment follows the deposition, the subsequent reduction in hydrogen has a smaller effect.

Similar behavior is exhibited by phosphorus-poisoned samples (Table 2). In the absence of oxygen the phosphorus covers the platinum, but it can be easily removed by a mild oxidation. The platinum surface is completely recovered although a large amount of phosphorus remains on the catalyst and is probably associated with the alumina.

TABLE 2
Titration of Phosphorus-Poisoned Samples

	H_2 uptake (μmoles H_2/g)		
Phosphorus added (w/w%)	Fresh (without poison)	After addition of poison	Treated by O_2 at 300°C
Red phosphorus			
0.07	3	Not measured	2.4
0.19	3	0.032	2.9
0.42	3	0.028	3.3
0.83	3	Not measured	2.8
0.09	0.4[a]	Not measured	0.4
P_2O_5			
0.68	3	0.074	2.5

[a] Presintered sample.

Such data could not have been obtained using conventional adsorption techniques, since the high-temperature reduction and evacuation that necessarily precede the adsorption would cause a major perturbation. This is very important in the examination of used automotive catalysts for hydrocarbon and CO oxidation, since they operate in an oxidizing atmosphere and a reduction prior to adsorption may alter the state of the platinum surface as shown above.

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