Surface Area of Platinum Catalysts

DETERMINATION OF METAL PARTICLE SIZE

A knowledge of the surface area of catalysts and other solids is important in the evaluation of their properties. The advent of the BET (Brunauer, Emmett and Teller) technique in the late thirties was a tremendous advance, but it has the great disadvantage that, since it employs physical adsorption, it is non-specific, and cannot in the case of a supported metal catalyst distinguish what fraction of the total area is due to metal and what fraction to the exposed support.

In two recent papers L. Spenadel and M. Boudart of the Esso Research and Engineering Company and S. F. Adler and J. J. Keavney of the American Cyanamid Company describe attempts to determine the specific surface area and average crystal size of platinum in low concentration (<1 per cent) platinum-alumina catalysts. The size of the metal particles present in such catalysts is less than can be estimated by the method of X-ray line-broadening (<50 Å). Estimation of the metal area is based on the measurement of the volume of hydrogen adsorbed by the catalyst at a high temperature, where adsorption on the support is small or negligible. The method is not entirely novel, and references to previous work are given. Both groups of workers agree that to obtain rapid adsorption it is necessary to pre-reduce catalysts in hydrogen at 500°C, following this by a prolonged period of pumping at the same temperature to remove adsorbed hydrogen. The monolayer hydrogen volume per gram of catalyst is given by the volume adsorbed in 0.5 to 0.75 hours at 240 mm and 250°C (1), or in two hours at 9 mm and 200°C (2). The use of the lower pressure at the lower temperature is permissible because the adsorption is stronger the lower the temperature. For fresh catalysts containing about 0.6 per cent platinum the volumes adsorbed were 15.2×10^{-6} moles (1) and 21.4×10^{-6} moles (2): the agreement is encouraging.

Now the former figure implies a platinum surface area of 273 $m^2 g^{-1}$, and that the ratio of adsorbed hydrogen atoms to platinum

The Effect of Heat Treatment on the Size of Platinum Crystallites on Impregnated Catalysts

Treatment	Diameter, Å		Reference
	By adsorption	By line-broadening	
2 hours at 650°C	61	200	1
24 ,, 650°C	212	255	1
24 ,, 750°C	253	255	1
5 ,, 705°C	18	200	2
5 ,, 750°C	290	275	2

atoms is 0.99. For this to be true, the platinum must be present either in "islands" of only one atom thickness, or in three-dimensional crystallites whose sides are less than two unit cells in length (1). Similar conclusions are drawn by the other group of workers. The effect of heat treatment on the particle size was also investigated, and some of the results are summarised in the table. The first three entries and the last two separately show that continued sintering gives progressively better agreement between the two methods of determination. The interpretation of this, given in similar terms by both groups, is that after a little sintering some of the platinum has grown to form large crystallites (recorded by line-broadening), while much of the platinum remains as small crystallites (undetected by line-broadening). This distribution of crystallite sizes is described as bimodal. The mean diameter found by adsorption is therefore the true one, the difference becoming progressively less as the number of small particles decreases.

The effect of carbon deposition and removal on particle size was also studied: carbon was deposited by causing the catalyst to operate in a reforming reactor. A one-day "coking" reduces the hydrogen adsorption of a catalyst by almost five times, even although sufficient carbon is present to cover only 5 per cent of the total catalyst surface. Carbon deposition must therefore occur principally on the metal. Regeneration was effected by heating in a muffle-furnace, and if this was done below 600°C little loss in hydrogen adsorption took place.

These papers have established the usefulness of measurements of hydrogen adsorption in the determination of the size of the elementary metal crystallites present in supported catalysts. G. C. B.

References

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Ruthenium, Rhodium and Iridium in Catalysis

A SYSTEMATIC SURVEY OF THE LITERATURE

The literature on both platinum and palladium as catalysts is very extensive, and these two metals are widely employed in a variety of reactions on a commercial scale. The catalytic properties of the other members of the platinum group of metals are by no means so fully appreciated, nor are they employed for this purpose to anything like the same extent. But scattered throughout the world's scientific literature are quite a number of records of research carried out with one or other of these metals as catalysts in many different types of reactions.

An admirable survey of this literature has now been prepared and published by the International Nickel Company Inc., New York, as an *Annotated Bibliography on Ruthenium, Rhodium and Iridium as Catalysts.* Compiled by Ann E. Rea and Marguerite Bebbington of the company's Development and Research Division, the bibliography contains more than three hundred abstracts of papers and patent specifications, covering the period from 1881 to mid-1959. They are arranged in sections dealing respectively with the hydrogenation of organic compounds, other reactions of organic compounds, reactions with inorganic compounds, and catalyst properties.

The variety of catalytic reactions for which these metals have been investigated is extremely wide, and the collection of this considerable amount of data into one carefully arranged volume will unquestionably provide a most useful source of information for chemists and chemical engineers concerned with reactions in which one or other of these metals may provide the most suitable catalyst.