405. *The Rôle of Supports in Catalytic Hydrogenation. Part I. Specific Effects of Various Oxide Carriers on the Activity of Platinum.*

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Zirconia and thoria have been found to act as highly active promoters when used as supports for platinum in the liquid-phase hydrogenation of cyclohexene at room temperature. The activity of the complex catalyst containing a fixed amount of platinum first rises to a peak value and then falls with increasing amount of the support, the peak activity corresponding, with zirconia, to about 16 times that of the unsupported platinum and, with thoria, to about 12 times this value. A similar study has also been carried out with less active supports, including chromium sesquioxide, ceria, thorium chromite, and magnesia. Electron-microscopic studies have also been made of the disposition of the platinum on the support. This has been found to occur centrally on the supporting granules.

Considerable evidence exists that the part played by supports in heterogeneous catalysis is in many cases a specific one, the activity of such catalysts being influenced by the chemical nature of the support, in addition to that given by simple surface extension.[1] In such cases the catalyst may be regarded as a system consisting of an association complex of the main metallic or other constituent with the support.

In the present work, a constant small concentration of metallic platinum on gradually increased amounts of various metallic oxides has been employed as a catalyst for the liquid-phase hydrogenation of cyclohexene at room temperature. Well-defined maxima in the activity of the complex catalyst, showing the specific part played by the support, have been obtained: further, the maximum activities occur at different ratios of support to platinum for each of the supports used; and the activation effect in the series of oxides taken decreases in the order $ZrO_2 > ThO_2 > Cr_2O_3 > CeO_2 > ThO_2,2Cr_2O_3 > MgO$. The catalysts used have in all cases been made without exposure to high temperatures.

A study of the disposition of the platinum on the more active supports has been made by electron-microscopic photographs, which show the presence of approximately centrally disposed platinum aggregates on the support grains: it appears reasonable to assume that the observed specially high activity occurs at the platinum–support interface.

Experimental

In most cases, the supports used consisted of pure specimens purchased as such; but chromium sesquioxide was prepared by the heating of small quantities of ammonium chromate, with precautions against sintering by the development of excessive temperatures. Thorium chromite was made by co-precipitation, from a mixed aqueous solution of thorium nitrate and chrome alum, by means of ammonia, followed by thorough washing and drying at 80°.

General Preparation of the Supported Platinum Catalysts.—A known amount of each support was suspended in 10 c.c. of water, and to this the calculated volume of a 1% aqueous solution of chloroplatinic acid and an excess of 40% aqueous formaldehyde were added. The volume was made up to about 75 c.c. with water, after which the system was boiled for 20 min. After being cooled, the residue was centrifuged, washed with water, and dried at 55°. During the boiling, thermal turbulence in the liquid was in most cases sufficient to keep the small amounts of the oxides evenly dispersed; but when several grams of the heavier oxides, zirconia and thoria, were used, stirring was employed to obtain a uniform suspension of the carrier. With magnesium oxide, there was some apparent formation of the hydroxide during the boiling, accompanied by a tendency to turbidity. In all cases, the product was friable after being dried.

The activity of the preparations was tested, at 20° and at atmospheric pressure, for the liquid-phase hydrogenation of cyclohexene (1 c.c.) in absolute alcohol (9 c.c.), in a mechanically

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[1] Hill and Selwood, *J. Amer. Chem. Soc.*, 1949, **71**, 2522.

driven hydrogenation shaker operating under standardised conditions. The reaction course was approximately linear; the volume of hydrogen absorbed in the first 4 min. of hydrogenation was taken as a measure of the activity of the catalyst.

FIG. 1.

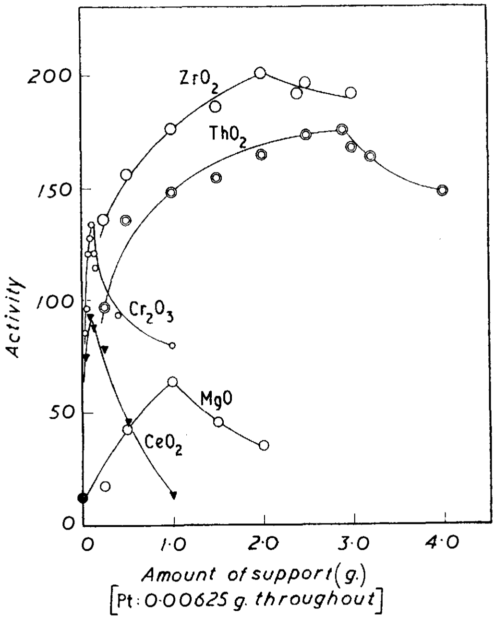
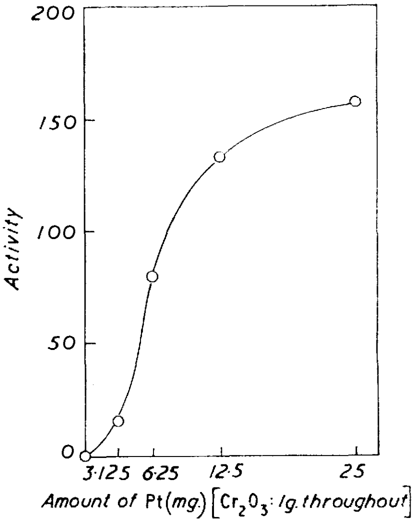


FIG. 2.



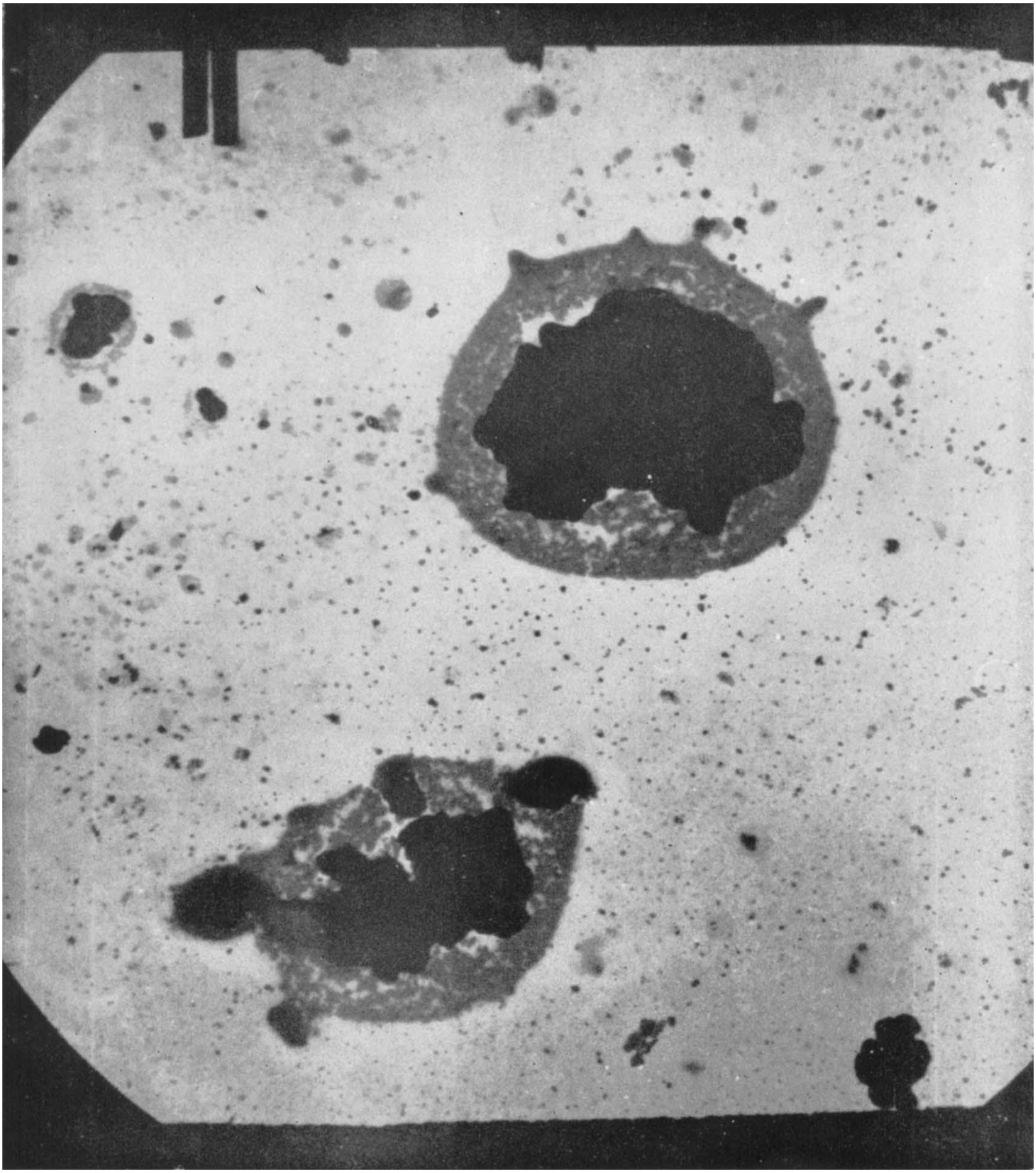
By working in this way, a fixed amount of platinum (0·00625 g.) was deposited on varying amounts of different supports, and the activity of each preparation determined. As a standard for reference, the activity of 0·00625 g. of unsupported platinum, prepared by reducing chloroplatinic acid in the absence of a support, was also measured.

TABLE 1.

Support	Amount of support corresponding to peak activity (g.)	Surface area of support (sq. m./g.)	Surface area of support corresponding to peak activity (sq. m.)	Ratio by weight of platinum to support at peak activity
MgO	1·0	40·0	40·0	$6·25 \times 10^{-3}$
$ThO_2,2Cr_2O_3$	0·15	58·6	8·8	$4·17 \times 10^{-2}$
CeO_2	0·1	45·0	4·5	$6·25 \times 10^{-2}$
Cr_2O_3	0·125	59·0	7·4	$5·00 \times 10^{-2}$
ThO_2	2·8	4·5	12·6	$2·23 \times 10^{-3}$
ZrO_2	2·0	5·85	11·7	$3·12 \times 10^{-3}$

The curves of Fig. 1, giving the results of this series, show that, with an increasing amount of each support, the activity first rises to a well-defined peak and then falls, giving in each case a typical promoter-action curve. These peaks occur at characteristically different catalyst-to-support ratios for each support (see also Table 1). The curve for thorium chromite has been omitted from Fig. 1 to avoid overcrowding. This curve rose sharply to a maximum value at 0·15 g. of the support, the activity corresponding to this peak being 88 on the scale of the Figure, and the fall beyond the peak being down to 53 at 1 g. of the support. With one of the supports, chromium sesquioxide, the set of experiments was repeated with twice the amount of platinum used previously (*i.e.*, 0·0125 g.). In this case, the peak in activity was obtained at exactly twice the amount of support needed previously (at 0·25 g. of chromium sesquioxide, in place of at 0·125 g.), *i.e.*, at the same ratio of platinum to support.

The surface areas of the supports, determined by the B.E.T. method with nitrogen at −183°, are given, the supports being arranged in order of increasing activity in Table 1. It will be seen



Platinum on zirconium dioxide, × 3500.

that there is no direct correspondence between the surface areas of these supports and their effectiveness. These results appear to indicate that some form of specific interaction between the more active supports and the platinum occurs. The very high promoting effects of zirconia and thoria are to be noted.

The influence of the area of the support is more clearly shown by the results of a further series of measurements in which varying amounts of platinum were deposited on a fixed amount (1 g.) of the same support (chromium sesquioxide). The results, given in Fig. 2, show that, as the amount of platinum dispersed on the chromium sesquioxide is increased, a slow rise in the rate of hydrogenation occurs, followed by a very rapid rise, and finally by a slower rise, apparently to a limiting value. This form of the curve is probably due to the fact that, in the initial stages, the very small amounts of platinum are too sparsely distributed on certain areas (see Plate) of the surface of the support for the two-point adsorption of cyclohexene to occur, in the manner postulated by Twigg and Rideal[2] for ethylene derivatives generally. However, as the amount of platinum is increased, the surface of the chromium sesquioxide becomes covered by platinum particles at a density more favourable for their effect on the reaction rate, and a relatively rapid increase in the hydrogenation velocity occurs. The addition of further amounts of platinum then becomes less efficacious, in the sense that there is unnecessary crowding of the platinum and ultimately the formation of multilayers of platinum particles on the chromium sesquioxide surface. The rate of hydrogenation accordingly then rises relatively slowly to a limiting value.

In the curves of Fig. 1 it will also be noted that, beyond the peak value, the rate at which the activity of the catalyst decreases with an increasing amount of the support varies widely with different supports. This, too, seems to be largely a simple surface effect; and this view is supported by the fact that, with chromium sesquioxide, cerium dioxide, magnesium oxide, and thorium chromite, the rate of fall after the peak is much greater than for zirconium dioxide and thorium dioxide, since the oxides of the former group, which have much larger surface areas per gram than the latter two oxides, will ultimately lead more rapidly to a too wide separation of the platinum grains for the necessary two-point adsorption of cyclohexene. Other factors are probably also operative, *e.g.*, differences in the porosity of the different supports, since it will be noted that for all the supports the rates at which the activities of the catalysts vary are not strictly proportional to the specific surface areas of these supports. With cerium dioxide, in particular, the activity diminishes very rapidly down to a negligible value.

As a preliminary example of a composite support, a trace of freshly precipitated thorium oxalate was mixed mechanically with 0·25 g. of chromium sesquioxide suspended in water ($Cr_2O_3 : ThO_2 = 100 : 0{\cdot}5$). This mixture was centrifuged, washed with distilled water, and then used as a support for 0·00625 g. of platinum. The activity of this catalyst was found to be twice that obtained if 0·25 g. of chromium sesquioxide alone was used.

Two cases of unfavourable interaction between platinum and a support, leading to the poisoning of the catalyst, were noted in work with vanadium pentoxide and basic thorium chromate. Three supported catalysts on vanadium pentoxide were prepared by the method already described, and their activities measured in the usual way. The results are given in Table 2. Here, increasing the amount of support causes, first, a decrease in the activity of the constant amount of platinum, owing to the toxic effect of the vanadium pentoxide, and then a gradual rise in the activity due to the general effects already discussed. Similarly, a sample of basic thorium chromate, prepared according to the method recommended by Britton,[3] was found, when used as a support, to poison the platinum completely, although both Th^{4+} and $(CrO_4)^{2-}$ ions, in solution, are known not to be toxic to platinum in hydrogenation catalysis.

TABLE 2.

Pt = 0·00625 g.

Amount of support (V_2O_5) (g.)	0	0·25	0·5	1·0
Activity (c.c. of H_2 absorbed in 4 min.)	12·5	8·5	11·7	18·9

Electron-microscopic Study of the Deposition of Platinum on Oxide Supports.—It has already been shown by Selwood and his co-workers,[4] on the basis of magnetic-susceptibility measurements, that the surface of two-component mixed-oxide catalysts, containing a small proportion

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[2] Twigg and Rideal, *Trans. Faraday Soc.*, 1940, **35**, 533.
[3] Britton, *J.*, 1923, **123**, 1429.
[4] Selwood and Lyon, *Discuss. Faraday Soc.*, 1950, **8**, 222.

of one of these oxides, consists of uncovered areas of the support, with intermittent superficial aggregates of the active oxide.

In the present work in which the amounts of platinum present are insufficient to cover the surface of the supporting oxide as a continuous layer, it has been found, on the basis of electron-microscopic photographs, that the platinum is present as more or less centrally disposed patches on the grains of the support, leaving bare surrounding areas of the support around these central regions. A typical electron micrograph of a zirconia-supported platinum catalyst, with a platinum-to-support ratio corresponding to the peak activity, is reproduced in the Plate, which shows the central dispositions of the platinum micro-aggregates, surrounded by a periphery of bare support.

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