808. *The Rôle of Supports in Catalytic Hydrogenation. Part I. Activation Effects of Various Oxide Carriers on Palladium.*

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Zirconia, thoria, alumina, and titania have been found to have a considerable activating effect when used as supports for palladium in the liquid-phase hydrogenation of cyclohexene in alcohol at 20° c. The activity of the supported catalyst, containing a constant amount of palladium, first rises to a peak value and subsequently falls as the amount of the support is further increased. This increase, with zirconia and thoria, amounts at the peak point to about 24 times the unsupported value, and with alumina and titania to about 22 times this figure. It was also noticed that, when different specimens of the same support were used, there was a marked difference both in the activities of the catalysts and in the location of the peaks in the graphs: further, in addition to the effect of the chemical nature of the support, the activity is also influenced by the surface area, by pore volume, and by other factors.

IN earlier work Maxted and Akhtar [1] have investigated the specific effects of various oxide supports on platinum, with special reference to differences in the activating effect of different oxides. In this part of the work a constant amount of metallic palladium was deposited, by reduction of the chloride with formaldehyde, on gradually increased amounts of various metallic oxides. The hydrogenation curves obtained, in addition to showing well-defined maxima in each case, showed that the activating effect, at the peak points of the oxides tested, decreases in the order: $ThO_2 = ZrO_2{}^{I} > Al_2O_3{}^{I} > TiO_2 > Cr_2O_3 > Al_2O_3{}^{II} > MgO > ZrO_2{}^{II} > V_2O_5$ (the index numbers on zirconia and alumina refer to different specimens of these oxides).

EXPERIMENTAL

The various supports used were of high purity and were used as purchased.

Preparation of Supported Palladium.—A known weight of each finely divided support was suspended in 50 c.c. of water, and a known amount of 1% palladium chloride solution was added. The mixture was shaken and set aside for 15 min., after which it was heated to its b. p. and formaldehyde (20 c.c.) and N/20-sodium carbonate solution (15 c.c.) were added. Reduction of the palladium chloride to palladium took place immediately, but the mixture was allowed to boil for 15 min. After this reduction, the mixture was cooled, centrifuged, washed with distilled water, and dried in an oven at 50°.

The activity of the supported catalysts was tested at 20° c and at atmospheric pressure, for the hydrogenation of cyclohexene (1 c.c.) in alcohol (9 c.c.), in a mechanically driven hydrogenation shaker operating under standard conditions, the volume of hydrogen absorbed in the first 4 min. being taken as a measure of the activity of the catalyst.

The small amount of hydrogen occluded by palladium alone in the presence of 9 c.c. of alcohol at 20° was also measured, by the same procedure as in the hydrogenation. It was found that 6 mg. of unsupported palladium occluded 0·2 c.c. of hydrogen in 4 min., and that supported palladium (the amount of the supports corresponding to the peak activity as in Fig. 1) occluded in each case 1·4 c.c. in 4 min. Any correction for occlusion was, however, not made in the figures, since the amount occluded was the same for all the supported catalysts and this amount is very small compared with the total volume of hydrogen absorbed in the hydrogenation of the cyclohexene.

RESULTS AND DISCUSSION

The results of a series of tests, involving the hydrogenation of cyclohexene and various supports, are summarised in Fig. 1, from which it will be seen that the activity of the various supported catalysts first increases to a well-defined maximum and subsequently

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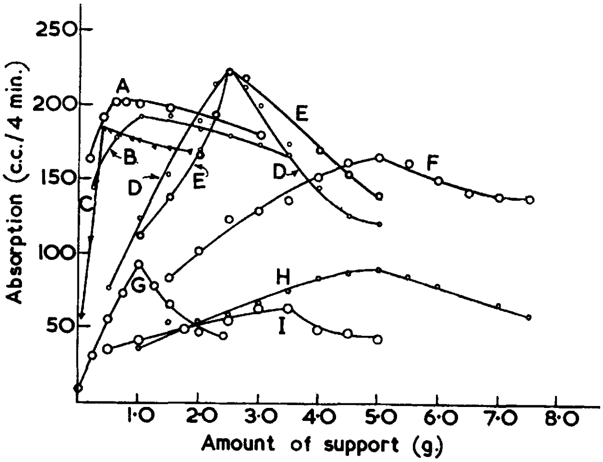
[1] Maxted and Akhtar, *J.*, 1960, 1995.

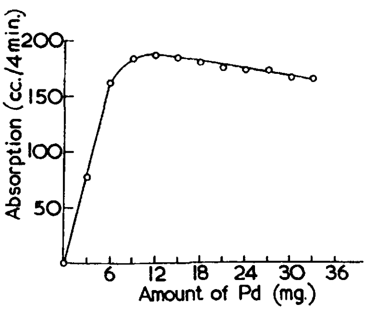
falls, the location of the peak being influenced by the nature of the support; further, these peak activities occur at different catalyst-to-support ratios for each support. A second coarse-grained sample of zirconia and alumina, of different origins, marked ZrO_2^{II} and $Al_2O_3^{II}$, was also tested. These supports gave curves differing in the location of their peaks from those given by ZrO_2^{I} and $Al_2O_3^{I}$. Fig. 1 also shows that the initial rise and subsequent fall in the activity, with all the catalysts tested, does not take place at the same rate, this being probably due to the specific effect of each of the individual supports and to differences in the pore and particle sizes, which determine the distribution of the catalyst on the support. In the case of very finely divided powders, such as alumina^{I}, titania, and chromium sesquioxide, the fall in the activity, after the peak point has been reached, is very slow; and it seems probable that the particles of the support, in such cases, may have shared a single palladium particle, and that this may be the cause of the subsequent slow fall in the activity.

FIG. 1. *Plots showing optimum proportions of support (palladium* = 0·006 g. *throughout).*



A, $Al_2O_3^{I}$. B, TiO_2. C, Cr_2O_3. D, ZrO_2^{I}. E, ThO_2. F, $Al_2O_3^{II}$. G, MgO. H, ZrO_2^{II}. I, V_2O_5.

FIG. 2. *Effect of varying the proportion of palladium on chromia* (0·5 g. *throughout*).



A second series of measurements was made with chromium sesquioxide, the amount of this support being kept constant at 0·5 g., and the total amount of the palladium being progressively increased. These results (Fig. 2) show that the activity of the catalyst first rises to a maximum value and then slowly falls. Under these conditions this subsequent fall in the activity is probably due to the overcrowding of the palladium particles on the surface of the support and especially on the covering of the active centres which are responsible for the activity.

In order to obtain some explanation of the increase in the activity of supported palladium, the surface areas of the various oxides used as supports were determined by the B.E.T. method,[2] by the adsorption of nitrogen at —183°. These are given in Table 1. The total pore volumes [3] of each oxide were also calculated, from the difference in the reciprocals of the bulk and the helium densities, the latter being derived during the B.E.T. measurements. The bulk density was measured by tapping the oxide powders in a graduated cylinder until a constant minimum volume was obtained, the mass of unit volume being taken as the bulk density.

It will be seen from Table 1 that there is, in general, no direct relationship between the gross surface area, the pore volume of the support, and the activity of the catalyst.

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[2] Brunauer, " Physical Adsorption of Gases and Vapours," Oxford University Press, 1944.

[3] Anderson, McCartney, Hall, and Hofer, *Ind. Eng. Chem.*, 1947, **39**, 1618.

The amount of the support required for the accommodation of 6 mg. of palladium at the peak ratio is far more than would be required even for a monolayer of palladium, although it is known that the catalyst does not occur on the surface of the support as a monolayer. It can be calculated that, if the palladium is deposited as a monolayer, the amount of the various supports required would be as also given in Table 1. It is obvious that other factors are involved in the distribution of the same amount of catalyst on various supports.

TABLE 1.

Support	Total pore volume (c.c. per g.)	Amount of support corresponding to peak activity (g.)	Surface area of support (sq. m. per g.)	Surface area of support corresponding to peak activity (sq. m.)	Wt. (g.) reqd. for monolayer of Pd *
ZrO_2^{I}	0·285	2·5	11·9	29·6	0·2532
ThO_2	0·279	2·5	20·9	52·3	0·1442
$Al_2O_3^{I}$	0·186	0·6	160·6	96·4	0·0187
TiO_2	0·639	1·0	95·5	95·5	0·0315
Cr_2O_3	0·364	0·4	45·6	18·3	0·0661
$Al_2O_3^{II}$	0·513	5·0	16·6	83·0	0·1815
ZrO_2^{II}	0·168	5·0	5·1	25·5	0·5900
MgO	0·608	1·0	24·2	24·2	0·1245
V_2O_5	0·490	3·5	4·6	16·1	$0·655_2$

* Calc. surface area for a monolayer of Pd = 3·014 m.^{2}.

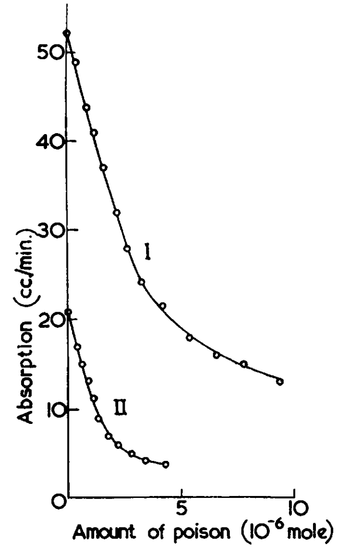

FIG. 3. *Effect of poisoning by dipentyl sulphide of palladium on zirconia.*
I, 6 mg. *of* Pd *on* 2·5 g.
II, 3 mg. *of* Pd *on* 2·5 g.

An attempt was made to determine the relative surface areas of the supported and of the unsupported catalysts. The method used involved poisoning, as had been employed by Maxted, Moon, and Overgage.[4] Dipentyl sulphide was used as a standard poison in all this series of measurements, it being presumed that preferential adsorption takes place on the palladium and not on the support.

The relationship used was $k_c = k_0(1 - \alpha c)$, in which k_c is the poisoned activity, k_0 the original activity, α the poisoning coefficient, and c the concentration of poison. If the surface area of one of the catalysts is known, that of other catalysts can be derived from the relation $\alpha_1/\alpha_2 = s_2/s_1$, in which s_1 and s_2 are the surface areas. The surface area of powdered metallic palladium was determined by the B.E.T. method, by the adsorption

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[4] Maxted, Moon, and Overgage, *Discuss. Faraday Soc.*, 1950, **8**, 135.

of nitrogen at −183°. The surface areas of other catalysts relative to that of metallic palladium were calculated by finding the value of α in each case.

The shape of the curves is given in Fig. 3. Here the linear (or almost linear) portion obtained was produced to cut the horizontal axis, which shows the concentration of the poison at which the value of $k_c = 0$. From this, $1 = \alpha c$. By inserting the value of α in each case, the relative surface areas of some supported catalysts (compared with that of metallic palladium) have been calculated: they are contained in Table 2.

TABLE 2. *Relative surface areas of supported catalysts.* (*Surface area of palladium determined by the B.E.T. method* = 33·7 m.^{2}/g. *Amount of palladium on each support* = 6 *mg.*)

Catalyst	$10^{-6}c$	$10^{6}\alpha$	Surface area (m.^{2})	k_0 (c.c./min.)
Palladium (0·025 g.)	3·5	0·290	0·842	12·0
Zirconia I (2·5 g.)	5·7	0·175	1·400	53·0
Zirconia I (2·5 g.) (3 mg. Pd)	2·4	0·417	0·58	21·0
Thoria (2·5 g.)	5·2	0·192	1·29	53·0
Titania (1·0 g.)	4·6	0·22	1·10	46·0
Alumina I (0·6 g.)	4·75	0·21	1·16	51·0
Alumina II (5·0 g.)	4·00	0·25	0·974	41·0
Zirconia II (5·0 g.)	4·1	0·244	1·000	21·0

It was found that if one-half (3 mg.) of the normal amount of palladium was used the calculated surface area was not one-half, this being also the case for the activity; and it seems probable that the excess of the support covers the surface of the palladium.

From these results it will be seen that the difference in surface areas of the catalysts on different supports is not as great as is the difference in the activity: further, in the case of alumina II and zirconia II, the difference in the activity is much greater, although the surface areas are almost the same. This shows that other factors are responsible for the increase in the activity. It is probable that the main centres of activity are not only on the catalyst proper, but also on the interfaces or points of contact between the catalyst and the support, and that these interfaces between different supports and the catalyst have different activities, dependent on the nature of the support.

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