

1007. *The Rôle of Supports in Catalytic Hydrogenation. Part II.*
Further Effects of Various Oxide Supports on the Activity of Platinum.*

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The relative activities of hydrogenation catalysts consisting of a constant amount of platinum supported on a varied amount of zirconia, alumina, or chromium sesquioxide have been determined, over a wide range of platinum-to-support ratios, for the liquid-phase hydrogenation of cyclohexene and ethyl crotonate. Values for the mean pore radii of these supports have been calculated from the respective specific surface areas and from micropore volume measurements, by using the B.E.T. nitrogen-adsorption and the mercury-penetration method. The difference in activity for the hydrogenation of cyclohexene and of ethyl crotonate is dependent on the mean pore radius, in addition to the nature of the support. This seems to imply that the pore factor is important, especially if the supported catalyst is used for the hydrogenation of a large molecule. The poisoning method described by Maxted, Moon, and Overgagge¹ has been used to estimate the relative surface areas of the supported platinum. Evidence, which cannot be accounted for by surface extension alone, is provided for the specific effects of supports.

THE present work continues that described in Part I.*

Experimental.—The catalysts used were prepared by allowing a known quantity of the various oxides to remain for 30 min. in contact with a dilute aqueous solution of chloroplatinic acid sufficient, after reduction, to give 6.25 mg. of metallic platinum. The suspensions were then stirred mechanically and heated to their boiling point and an excess of 40% formaldehyde solution was added. After 15 min. the supported platinum was centrifuged off, washed, and dried at 50°.

The hydrogenation tests were carried out at 20° and at atmospheric pressure, in alcoholic solution in a mechanically driven hydrogenation pipette, the charge of catalyst consisting in each case of 6.25 mg. of platinum carried on a varied amount of each of the supports. The system hydrogenated contained 1 c.c. of cyclohexene (or 1.5 c.c. of ethyl crotonate) dissolved in sufficient ethyl alcohol to give a total volume of 10 c.c. It was not found necessary to purify the cyclohexene; but it was found that the hydrogenation rate of ethyl crotonate was raised by a maximum of 5% by shaking this twice with reduced nickel supported on kieselguhr. The course of the hydrogenation was approximately of zero order; and the hydrogenation rate in c.c. per minute, reduced to N.T.P., was taken as a measure of the activity of the catalyst used.

The poisoning experiments were carried out in a similar way to the activity measurements

* Part I, *J.*, 1960, 1995.

¹ Maxted, Moon, and Overgagge, *Discuss. Faraday Soc.*, 1950, **8**, 135.

for the hydrogenation of cyclohexene, except that the system contained a known amount of the poison, ethyl sulphide. The hydrogenation was of almost zero order during the first few minutes; and the rate over this period was taken as a measure of the poisoned activity.

The B.E.T. surface areas were determined from adsorption isotherms with purified nitrogen at -183° , the cross-sectional area of a nitrogen molecule being taken as 15.4 \AA^2 . Micropore volumes were calculated from helium density measurements, on spectroscopically pure helium, and from mercury density measurements, which were made ² at a pressure of 1000 mm.

Results and Discussion.—Plots of the catalytic activities against increasing areas of the various supports, carrying a constant amount of platinum, are given in Fig. 1 for the hydrogenation of cyclohexene, and in Fig. 2 for the corresponding hydrogenation of ethyl crotonate, the relative activity of 6.25 mg. of unsupported platinum being shown by a single point at zero on the support-area axis. It will be seen that zirconia and the specially fine-grained specimen of alumina-I (of a size passing completely through a 200-mesh sieve) were by far the most active supports tested. The activity was also dependent to a large degree on the particle size of each of the supports, as well as on their chemical nature. Thus, a large-grained alumina (alumina-II; 100–200 mesh) gave a far less active catalyst than alumina-I, with, however, the peak activity in approximately the same position along the support-area axis. It will also be seen that, as would be expected, the position of the peak activity along the horizontal axis was independent of the substance hydrogenated.

The curves for zirconia and chromia rise relatively rapidly, and those for alumina much less steeply, to a peak point, after which the fall in activity is slower than the initial rise. Zirconia is the most active support for both reactions and raises the activity to nearly 22 times its unsupported value for the hydrogenation of cyclohexene, and to about 16 times this figure for the hydrogenation of ethyl crotonate.

From the ratio of platinum to support at the peak activity, it can be shown ³ that the platinum occupies a very small fraction (less than 4%) of the carrier surface. The absolute surface area of the platinum was not known; but an approximate value of the percentage coverage can be obtained if it is assumed that the platinum is dispersed to its fullest extent, *i.e.*, as a monatomic layer. The real coverage will be considerably less than this approximate value, since it is known that the platinum is present on the surface of the carrier as crystallites and would accordingly occupy a much smaller fraction of the surface than if it were present as a monolayer.⁴

The calculated weight of support necessary to accommodate a monolayer of 6.25 mg. of platinum is compared in Table 1 with that at the peak activity. The ratio of the calculated weight of support to that at the peak activity gives the coverage, or the ratio of the area of a monolayer of platinum to that of the support at the peak activity.

TABLE 1.

Support	Calc. wt. of support reqd. for monolayer dispersion of platinum (g.)	Wt. of support at peak activity (g.)	Calc. coverage (%)
Al ₂ O ₃ -I	0.0072	0.65	1.16
Cr ₂ O ₃	0.0245	0.75	3.23
Al ₂ O ₃ -II	0.0753	6.0	1.25
ZrO ₂	0.0993	2.25	4.41

The initial rise in the activity curves is probably due to two causes. If the amount of the support is small, the whole of the chloroplatinic acid may not be adsorbed from the solution during the preparation of the catalyst, so that, on reduction, some of the platinum

² Juhola and Wiig, *J. Amer. Chem. Soc.*, 1949, **71**, 2078.

³ W. B. Innes, "Catalysis," ed. P. M. Emmett, Reinhold Publ. Corp., New York, 1954, Vol. I, p. 258.

⁴ Maxted and Akhtar, *J.*, 1960, 405, 1995.

is reduced to the metallic state in the solution rather than on the support. Alternatively, complete adsorption of the chloroplatinic acid by small amounts of carrier might lead to large crystallites of platinum, as a result of the close proximity of the adsorption sites of PtCl_6^{2-} ions on the carrier surface, before reduction. As the amount of support is increased, with a constant weight of platinum, either more platinum is formed on the support, or that which is formed consists of smaller crystallites. It was possible to distinguish unsupported from supported platinum by the dense black colour of the former, and by the difficulty in its separation by centrifugation. Even with large amounts (up to 4 g.) of alumina-II (100—200 mesh), some unsupported platinum was formed.

The reasons for the fall in activity may also be of two sorts: namely, (i) the platinum crystallites may be so small that the two-point adsorption of the unsaturated molecule on a single crystallite of the platinum becomes impossible, or (ii) an excess of bare support may cover areas of the supported metal and in this way hinder the free diffusion of reactant molecules to, and of molecules of product from, the active surface. If (i) is correct, the specific surface area of the platinum should continue to increase as the amount of the support is increased; whereas, if (ii) is correct, the most active catalysts should have a maximum available surface of platinum.

Plots of the poisoned activity, k_c , for each supported catalyst against the total poison present are linear for small quantities of poison and may be represented¹ by the equation $k_c = k_0(1 - \alpha c)$, in which k_c is the activity in the presence of c moles of poison, k_0 is the unpoisoned activity, and α is the poisoning coefficient, which is inversely proportional to the surface area. If c_0 is the value of c when $k_c = 0$, then $\alpha = 1/c_0$, and c_0 , the intercept of the extrapolated linear plot with the poison concentration axis, is proportional to the surface area of the platinum.

There is no direct dependence of the activity of the peak amount of each support (italicised in Table 2), on the surface area of the supported platinum, represented by the values of c_0 in Table 2, since the platinum supported by zirconia has a smaller relative

TABLE 2.

Support	Amount (g.)	k_0 (cyclohexene) (c.c. of H_2 absorbed per min.)	c_0 (10^{-7} mole)	$k_0\alpha$ (10^7 c.c. per min. per mole)
ZrO ₂	2.25	45.5	9.5	4.8
Al ₂ O ₃ -I	0.05	35.0	12.2	2.9
	0.30	42.0	13.4	3.1
	0.60	44.8	14.0	3.2
	0.75	41.7	13.2	3.2
	1.00	39.5	12.8	3.0
Cr ₂ O ₃	0.75	38.7	12.5	3.1
Al ₂ O ₃ -II	6.00	18.8	8.9	2.1

surface than that supported by alumina-I, although their activities are almost the same. If the activity of these catalysts were dependent only on the surface area of the platinum, the respective values of $k_0\alpha$ would be the same for each support. Actually they are different, which indicates that the effect of each support is specific, the specificity being most marked in the case of zirconia.

The relative surface area of platinum supported by different amounts of alumina-I does not continue to increase as the amount of support is increased beyond that required for maximum activity, but falls as the activity decreases. Accordingly factor (ii), put forward above for the fall in activity, outweighs any effects due to (i).

When a metal is deposited on a porous support, some of the active surface becomes unavailable for catalysis by being contained in pores. Even if the mean pore radius is large compared with the size of the reacting molecules, the activity may, for the following reasons, be decreased by this deposition of platinum in the pores. The growth of platinum crystallites may occur across the mouth of a pore, in such a way as to block the entry of

molecules of reactant to the platinum which has been deposited with the pore. Further, the pore radius may be substantially reduced by the thickness of the metal layer on the internal surface of the pore; and, according to the size and shape of the pore and of the potentially adsorbable molecule, diffusion of reactant or resulting molecules to or from the active surface will be inhibited to a greater or lesser degree.

The use of a carrier with small pores to support the platinum would accordingly be expected to lead to a decreased activity, compared with that of the same amount of platinum of equal surface area deposited on a non-porous carrier, owing to the unavailability to a large molecule of part of the internal catalyst surface, the extent of the decrease in activity becoming greater the smaller the mean pore radius and the larger the unsaturated

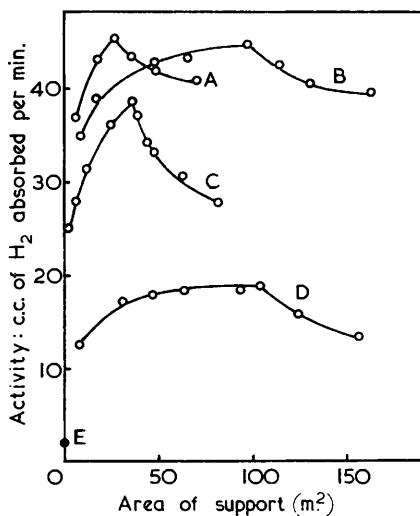


FIG. 1. Hydrogenation of cyclohexene.

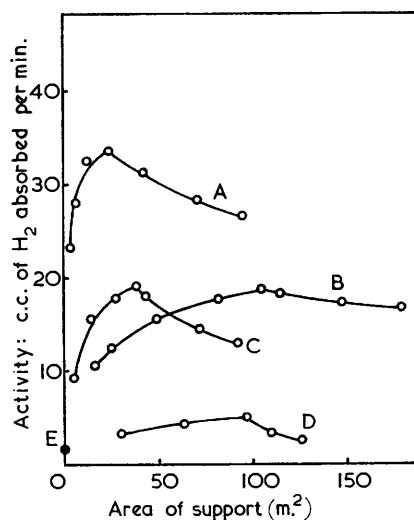


FIG. 2. Hydrogenation of ethyl crotonate.

Key (for both Figs.): A, ZrO_2 ; B, Al_2O_3 -I; C, Cr_2O_3 ; D, Al_2O_3 -II; E, unsupported Pt.

molecule hydrogenated. For these reasons, the activity of a given weight of platinum on a porous carrier, when this is used for the hydrogenation of unsaturated molecules of different molecular sizes, would be expected to differ owing to this difference in the molecular size, as well as to any difference due to the chemical nature of the molecule hydrogenated. Further, this difference would depend to some degree on the mean pore radius of the carrier. The difference in the activity of each of the supported catalysts used for the hydrogenation of cyclohexene and of ethyl crotonate has been compared in Table 3 with the mean pore radius of the respective supports.

TABLE 3.

Support	Al_2O_3 -I	Cr_2O_3	Al_2O_3 -II	ZrO_2
Mean pore radius (Å)	21	136	224	382
Activity difference for cyclohexene and ethyl crotonate at the peak ratio (c.c. per min.)	26.0	20.0	13.8	11.8

It will be seen from Fig. 1 that zirconia and alumina-I have almost the same activity at their peak ratios for the hydrogenation of cyclohexene, whereas, for the corresponding hydrogenation of ethyl crotonate, there is a wide difference in their activities. It is evident that the two supports are equally active for the hydrogenation of the smaller molecule, and that the fine pore structure of alumina-I is the cause of its relatively lower activity, compared with that of zirconia, for the hydrogenation of the larger molecule of

ethyl crotonate. The evidence for the influence of the pore size of the carrier on the activity of the platinum is confirmed by the values in Table 3. The reduction in the active surface available for catalysis, represented by the figures in the second column, corresponds with the mean pore radius of the support. Accordingly, the greatest difference in activity occurs in the case of alumina-I, which has the smallest pore size, whereas the smallest difference occurs for a zirconia-supported catalyst, which has the largest pore size. Chromium sesquioxide and alumina-II have activity differences which lie between those of alumina-I and zirconia and, for each of these carriers, the activity difference is less for the support with the greater mean pore radius.

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