214. *The Role of Supports in Catalytic Hydrogenation. Part II. Activation Effects of Various Metallic Oxide Carriers on Palladium, with Relation to the Magnetic Susceptibility and Adsorption Capacity of the Catalyst, and Studies on the Sintering of Palladium Catalysts.*

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In the first part of this work an attempt has been made to correlate the activity, for the hydrogenation of cyclohexene at 20°, of palladium catalysts, on various metallic oxide supports with their magnetic susceptibilities and with their adsorption capacity for ethylene as a monolayer. We have found that, in the case of some supports, an increase in paramagnetic character favours an increase in catalytic activity, whereas in other cases, *e.g.*, chromium sesquioxide and nickel oxide, no direct correspondence between activity and paramagnetic susceptibility has been observed. This is probably due to the strong paramagnetic nature of these supports themselves. It has been found that with an increase in the amount of palladium on a fixed amount of the support, the paramagnetic susceptibility increases continuously, whereas the activity increases up to a certain concentration of palladium, above which it begins to decrease. In the case of mixed supports, an increase in catalytic activity is found to be related to an increase in paramagnetic susceptibility, except for chromium sesquioxide and nickel oxide which show their own strong paramagnetic nature.

In another part of the work we have studied the effect of the sintering of supported palladium catalysts on their activity for the hydrogenation of cyclohexene at 20°. It was found that after sintering: (i) in some cases the loss in activity was smaller the greater the mean pore size of the supports; (ii) as the concentration of palladium on the support was increased, the percentage decrease in activity rose; (iii) on increasing the temperature and time of sintering, a linear decrease in activity was observed up to a limit after which the activity change was very small. It was also found that sintering in the presence of a stream of gas gave more closely comparable results than sintering in air or in a vacuum.

IN earlier work, Selwood [2] found that, for a number of catalysts, a close connection exists between the magnetic susceptibility and the catalytic activity. Selwood [3] also found that the chemisorption of ethylene on metallic catalysts at 28°, and above, takes place by a

[1] Part I, Maxted and Ali, *J.*, 1961, 4137.
[2] Selwood and Eischens, *J. Amer. Chem. Soc.*, 1947, **69**, 1590, 2698; 1948, **70**, 2271; Selwood and Dallas, *ibid.*, 1948, **70**, 2145; Selwood, Ellis, and Wethington, *ibid.*, 1949, **71**, 2181; Selwood and Lyon, *ibid.*, 1952, **74**, 1051; Selwood and Mooi, *ibid.*, 1952, **74**, 175; Selwood, Moore, Ellis, and Wethington, *ibid.*, 1949, **71**, 693; Selwood and Mooi, *ibid.*, 1950, **72**, 4333.
[3] Selwood, *J. Amer. Chem. Soc.*, 1957, **79**, 3346; 1961, **83**, 2853.

partial dissociation, *e.g.*, with the formation of $CH_2 \cdot CH \cdot$ and $H \cdot$, and that the self-hydrogenation of ethylene to ethane also occurs, as observed by Beeck [4] and Trapnell.[5] Schwab and his co-workers [6] used alumina " doped " with various *p*- and *n*-type semiconductors as nickel catalysts in order to change the electron concentration in the catalyst by metal-semiconductor contact, and they found that by doping with a *p*-type semiconductor, the activation energy of the catalyst for the decomposition of formic acid was decreased and the paramagnetic susceptibility increased, whereas by doping with an *n*-type semiconductor, the activation energy was increased and the paramagnetic susceptibility decreased. Agronomov and Mardasher [7] found that an increase in the concentration of the catalyst on a carrier, beyond a certain limit, leads to a gradual decrease in the catalyst surface and hence the catalytic activity.

Adler and his co-workers [8] found that platinum on alumina is in a highly dispersed state and sometimes in an ionic form, and that heat treatment causes the formation of platinum crystallites and also the loss of the catalyst surface by the interconnection of the adsorption sites. Selwood and his co-workers [9] have found that a minimum particle size, or " domain," is necessary for a particular reaction and that an increase or decrease of a catalyst on the support, beyond a certain limit, leads to a gradual fall in the activity, this being in agreement with the work of Balandin.[10] •

EXPERIMENTAL

The various single supports were of high purity and were used as purchased. In the case of mixed supports, magnesium oxide was used as such, and its concentration kept constant; this support was used together with other second supports, *e.g.*, with cerium dioxide, thorium dioxide, chromium sesquioxide, and nickel oxide. These second supports were made from their nitrates, and in the case of chromium sesquioxide from ammonium chromate, by decomposition at 550—650° in the presence of moisture. The mixed supports were finely ground, well washed with water, and dried at 100°. Unless otherwise stated, the mixed supports were made up of 50% of each of the components. It was then found that magnesium oxide particles were almost completely covered by a layer of the second support. The palladium (6 mg.) was deposited on the supports (1 g.) by the method previously reported.[1] The catalysts were dried at 110° for 24 hr. The surface areas of the single supports were known from our previous work.

The adsorption of ethylene at 20° was measured by use of the apparatus that had previously been used for surface-area determinations. The catalysts were first evacuated for 8 hr. at room temperature and then for 4 hr. at 180°, the pressure being 10^{-6} mm. Adsorption readings were taken every 30 min. after the admission of ethylene. The values of V_m, the volume of ethylene required to give a complete monolayer, for each catalyst were calculated by a B.E.T. plot for each 10 g. of catalyst.

The magnetic susceptibilities (χ), were measured by use of the Gouy method at 20° and are quoted for 1 g. of catalyst. For these measurements the catalysts were first evacuated at 180° for 4 hr. at 10^{-6} mm., in order to remove any adsorbed gas, before being sealed off.

The activities of the catalysts, which had been previously treated for 4 hr. at 180° followed by cooling, were found to be uniform over a long period. The activities of the original catalysts without heat treatment were also measured for comparison. The hydrogenation charge contained the catalyst (1 g.), cyclohexene (2 c.c.), and ethanol (10 c.c.). The hydrogenation activity for the first 5 min. was taken as a measure of activity.

For the studies of sintering, the catalysts were dried for 24 hr. at 100°. The mean pore sizes of each support were calculated from the formula, $d = 4V/A$, *d* being the diameter in Å, *A* the

[4] Beeck, *Discuss. Faraday Soc.*, 1950, No. 8, 118.
[5] Trapnell, *Trans. Faraday Soc.*, 1952, **48**, 161.
[6] Schwab, Block, and Schultze, *Angew. Chem.*, 1959, **71**, 101; Schwab, *ibid.*, 1961, **73**, 399.
[7] Agronomov and Mardasher, *Russ. J. Phys. Chem.*, 1961, **35**, 819.
[8] Herrmann, Adler, Goldstein, and de Braunn, *J. Phys. Chem.*, 1961, **65**, 2189; Adler and Kearney, *ibid.*, 1960, **64**, 208.
[9] Selwood and Mooi, *J. Amer. Chem. Soc.*, 1952, **74**, 2461; Selwood and Hill, *ibid.*, 1949, **71**, 2522.
[10] Balandin, *Z. phys. Chem. (Leipzig)*, 1929, B, **2**, 289.

surface area, and V the mean pore volume. The total pore volume of each support was calculated from the difference in the reciprocals of the bulk and the helium densities, the latter being determined during the surface-area measurements. The sintering experiments were carried out in a stream of hydrogen having a flow-rate of *ca.* 200 c.c./min., the samples being cooled in a hydrogen atmosphere. For comparative purposes, some sintering experiments were carried out in the presence of air, and others at a pressure of 10^{-5} mm. The furnace temperature was controlled by a thermocouple. Sintering was carried out in the reaction pipette itself which had an inlet and an outlet, the inlet tube touching the bottom of the pipette so as to ensure a homogeneous atmosphere of hydrogen. After being cooled, the catalyst (1 g.) was covered with cyclohexene (3 c.c.) and ethanol (10 c.c.); the hydrogenation activity for the first 10 min. was taken as a measure of the activity, which was uniform over a considerable time.

Results and Discussion

In the first part of this work, the activation effects of various metallic oxide supports on palladium, with relation to the magnetic susceptibility and the adsorption capacity for ethylene as a monolayer, have been studied, and are summarised in Table 1. It is seen that with an increase in the paramagnetic character of the catalyst, the activity is also increased; however, in the case of palladium on chromium sesquioxide, the high paramagnetic character observed is due to the paramagnetic nature of the support and does not appear to relate to the activity of the catalyst. This may be due to the low electron concentration which appears to favour strong adsorption, the adsorbate molecules not being released in the case of rapid hydrogenation reactions. The values of V_m for the catalysts do not appear to relate to their catalytic activity, and there is no great variation except in the case of palladium/chromium sesquioxide, this being probably due to the p-type conductivity of the support. The variation in activity of palladium, on various supports, was previously [1] found not to be due to the change in the surface area of the catalysts, but to the particular nature of the support itself.

In continuation of this work, we have studied the effect of increasing the concentration of palladium on a constant amount of support. The relative values obtained are summarised in Table 2.

Table 1.

(6 mg. of Pd per g. of support).

Support	Original activity *	Activity * after being heated at 180°	χ (per g.)	V_m (c.c./10 g.)	Surface area of supports (m.²/g.)
ZrO₂	254	231	$+0.78 \times 10^{-5}$	7.86	11.9
ThO₂	225	215	$+0.52 \times 10^{-5}$	8.61	20.9
Cr₂O₃	182	168	$+19.6 \times 10^{-5}$	16.26	45.6
Al₂O₃	109	104	$+0.16 \times 10^{-5}$	6.00	16.6
MgO	93	84	$+0.08 \times 10^{-5}$	10.23	24.2
TiO₂	197	178	$+0.21 \times 10^{-5}$	7.22	95.5

* In c.c. of hydrogen per 5 min.

Table 2.

(1 g. of ThO₂ throughout).

Pd (mg.)	Original activity *	Activity * after heating at 180°	χ (per g.)	V_m (c.c./10 g.)
6	225	215	$+0.52 \times 10^{-5}$	8.61
12	268	248	$+1.76 \times 10^{-5}$	10.01
24	283	262	$+6.12 \times 10^{-5}$	12.21
36	276	248	$+9.72 \times 10^{-5}$	13.26
48	270	244	$+11.7 \times 10^{-5}$	13.46

* Cf. Table 1.

It is seen that with a given increase in the palladium content of the catalyst, the activity does not increase to the same degree, but decreases slightly after reaching a certain

TABLE 3.

(6 mg. Pd per g. support).

Supports †	Original activity *	Activity * after heating at 180°	χ (per g.)	V_m (c.c./10 g.)
MgO alone	93	84	$+0\cdot082 \times 10^{-5}$	10·22
MgO + CeO$_2$	218	196	$+0\cdot58 \times 10^{-5}$	10·80
MgO + ThO$_2$	198	186	$+0\cdot15 \times 10^{-5}$	11·20
MgO + Cr$_2$O$_3$..............	168	154	$+69\cdot0 \times 10^{-5}$	14·27
MgO + NiO (50%)	158	144	$+93\cdot0 \times 10^{-5}$	91·42
MgO + NiO (8%)	172	161	$+22\cdot0 \times 10^{-5}$	13·60

* Cf. Table 1. † Unless otherwise stated, the mixed supports were of 50% of each of the components.

palladium : support ratio. The paramagnetic character increases continuously, as was observed by Trzebiatowski [11] who found that, in the case of palladium, the susceptibility increased with an increase in the concentration, whereas, with platinum, the susceptibility became constant at very low dilution. V_m increases rapidly up to a certain limit, after which the increase is very slow; this slow increase can be attributed to a slow chemisorption process, due to the generation of new active sites on the catalyst surface.

We have also used mixed supports for the palladium catalyst; the results are summarised in Table 3.

It is seen that cerium dioxide and thorium dioxide, as second components, provide the most active catalysts, although the paramagnetic characters are fairly low. There is very little variation in V_m, except for chromium sesquioxide and nickel oxide, this being probably sue to the p-type conductivity of these supports. When only 8% of nickel is used, the catalytic activity is increased to a greater extent than with 50% of nickel oxide, although the paramagnetic susceptibility and V_m are not as great.

In another series of experiments, sintering studies have been made for palladium catalysts on various supports of different pore size, with a constant palladium : support ratio. The sintering was carried out at 350° for 4 hr. The results are summarised in Table 4. The relationship of the percentage decrease in activity to the pore size of the support is shown graphically in Fig. 1.

TABLE 4.

(12 mg. of Pd per g. of support).

Support *	Original activity *	Activity † after sintering	Average pore size (Å)	Percentage decrease in activity
ZrO$_2$...........................	568	387	94	32·0
ThO$_2$	550	370	54	32·5
Al$_2$O$_3$	278	217	123	22·0
MgO...........................	212	151	100	29·0
Cr$_2$O$_3$	404	251	32	38·0
TiO$_2$...........................	454	236	26	48·0

* For surface area of supports, see Table 1.   † In c.c. of hydrogen per 10 min.

It is seen from Table 4 that, in some cases, the greater is the pore size, the smaller is the fall in activity. In the case of chromium sesquioxide and titanium dioxide the rate of decrease of activity is the highest, this being probably partly due to the small pore sizes and partly to the high surface areas which more easily allow the agglomeration of the minute particles. It is probable that metallic-particle growth occurs inside the pores during sintering, so that the pore mouths are blocked against the entry of the adsorbate molecules, thus reducing the active surface. In the case of supports of larger pore size, the crystallites formed probably do not completely block the pores and there still remains some space for the entry of the adsorbate molecules, although the number of active centres is reduced.

[11] Trzebiatowski, *Problem. Kinetika i Kataliz Akad. Nauk. S.S.S.R.*, 1960, 155.

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We have also gradually increased the amount of palladium and kept the amount of support constant, the sintering being carried out for 4 hr. at 350°. The results are summarised in Table 5.

TABLE 5.

(ThO$_2$: 1 g. throughout).

Amount of palladium	6 mg.	12 mg.	24 mg.	36 mg.	48 mg.
Original activity *	450	550	636	612	602
Activity * after sintering	333	363	410	356	334
Percentage decrease in activity	27	33	36	42	44

* C.c. of hydrogen per 10 min.

It is seen that the fall in activity gradually increases with increase in palladium content. This may be due to the ease of formation of larger crystallites owing to the closer dispersion
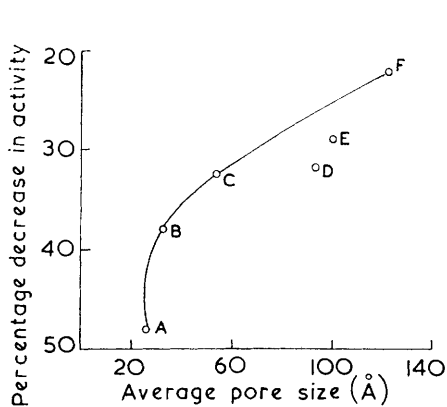

FIG. 1.   Effect of the average pore size of the supports on the percentage decrease in activity of a palladium catalyst (12 mg. of Pd per g. of support) after being sintered at 350° for 4 hr.   Support: A, TiO$_2$; B, Cr$_2$O$_3$; C, ThO$_2$; D, ZrO$_2$; E, MgO; F, Al$_2$O$_3$.
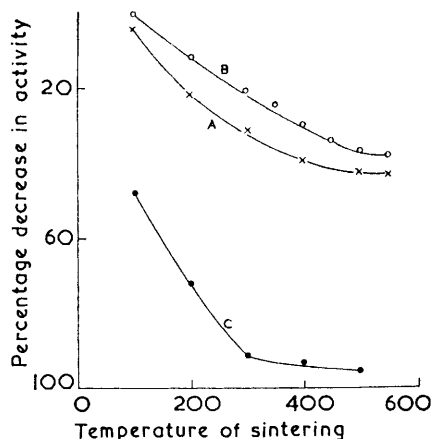

FIG. 2   Effect of increasing the sintering temperature on the percentage decrease in activity of a palladium catalyst (12 mg. of Pd per g. of ThO$_2$ support) sintered for 4 hr. at the temperatures shown.   A, in hydrogen.   B, in air.   C, in a vacuum (10^{-5} mm.).

of palladium particles. The original activity increases up to a certain concentration of palladium and then begins to decrease.

We have also gradually increased the time of sintering at constant temperature and palladium : support ratio. The results are given below.

Temperature = 350°; Pd/Support = 12 mg. per g. ThO$_2$; original activity (2 hrs. sintering) = 550 c.c. H$_2$ per 10 min.

Percentage fall in activity	29	33	36	40	42	42
Time of sintering (hr.)	2	4	8	12	16	20

It is seen that, with an increase in the time of sintering, the decrease in activity is very rapid up to about 2 hour after which it is relatively slow.

The effect of increasing the sintering temperature for a catalyst having a constant palladium : support ratio is summarised graphically in Fig. 2. It is seen that the decrease in activity for both A and B is very rapid up to 400°, the subsequent decrease being very slow. The decrease in activity with increase in temperature is not linear; it is probable that most of the agglomeration occurs below 400°, and that, with a further increase in temperature, the larger crystallites formed remain at a favourable distance apart, when

agglomeration takes place to a lesser extent. For sintering in a vacuum (C), it is seen that the decrease in activity is very rapid, the activity being only 8 and 4%, respectively, of its original value at 300 and 500°.

Conclusion.—From the first series of experiments, we conclude that the values of V_m for various catalysts cannot be correlated with their activities in the case of fast reactions, particularly when the supports have themselves some adsorbing power for the unsaturated molecules, and that a given relationship between activity and paramagnetic susceptibility only holds up to a certain concentration limit, especially in the case of palladium, at which the paramagnetism is observed to increase continuously with increasing concentration, whereas the activity begins to decrease above this concentration. The catalytic activity of palladium on various supports can, only in a few cases, be correlated with the paramagnetic susceptibility, there being no correlation when the support itself has a strong paramagnetic nature. Cerium dioxide or thorium dioxide, together with magnesium oxide as a mixed support, gives the highest activity and also slightly increases the paramagnetism of the catalyst. This, we believe, is due to the slight paramagnetic nature of these supports themselves, and has been observed earlier by Rienaecker and Yuch Wu.[12]

From studies of sintering, we conclude that the decrease in activity of palladium catalysts on supports having large pores is less than that on supports having small pores; this is probably due to the blocking of the pores by the formation of larger crystallites and to the stopping of the free entry of the adsorbate molecules. The fall in activity also increases with increase in (i) palladium content, (ii) temperature of sintering, and (iii) the time of sintering, but only up to a certain limit, after which the change is very small, this being probably due to the formation of larger crystallites which remain at a favourable distance apart, so that further agglomeration occurs only to a small extent. After sintering in a vacuum, the decrease in activity is very fast, probably owing to the absence of gas which would keep the catalyst particles in an activated state and apart; thus, the palladium particles combine more easily, with the formation of a network of larger crystallites and with a reduction in the active surface.

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[12] Rienaecker and Yueh Wu, *Z. anorg Chem.*, 1962, **315**, 121 (*C.A.*, 1962, **57**, 9268).