447. *The Activation of Platinum Catalysts by Rare-earth and Other Oxides in the Decomposition of Hydrogen Peroxide.*

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Various authors have used semiconductors and insulators such as charcoal, silica gel, and alumina gel as promoters for the decomposition of hydrogen peroxide by platinum catalysts. Lebeder and Trosman [1] have used cadmium oxide as a support. In the present work, it has been found that small quantities of metallic oxides, mainly of the rare-earth type and including thoria, zirconia, chromium sesquioxide, magnesia, titania, vanadium pentoxide, lanthanum sesquioxide, praseodymium oxide, thallium sesquioxide, and samarium sesquioxide, act as strong promoters in the decomposition of aqueous hydrogen peroxide by finely-divided platinum at 20° and at normal atmospheric pressure. In general the activity of a constant amount of platinum first rises to a peak point and subsequently sinks as the ratio of promoters to platinum is further increased. The order of the activities of these promoters follows the sequence: $ThO_2 > ZrO_2 > Cr_2O_3 > CeO_2 > MgO > TiO_2 > V_2O_5 > La_2O_3 > Pr_6O_{11} > Tl_2O_3 > Sm_2O_3$. The degree of activation is in many cases considerable, being almost nine times the unpromoted value for thoria and zirconia at the peak point in the activity curves.

THE supported platinum used in all the activity measurements was 7·99 mg. and was made by the reduction, by aqueous formaldehyde, of the equivalent amount of chloroplatinic acid on various amounts of these oxide supports.[2] The platinum was precipitated on the various supports by heating the contents in a small beaker, with stirring in order to obtain an even distribution. In spite of the extreme dilution of the acid in the solution, the reduction was obtained in a few seconds as was shown by the darkening of the oxide. The precipitate was centrifuged, thoroughly washed with hot distilled water and dried at 50°. The apparatus employed throughout is shown in Fig. 1. It consists of a glass reaction vessel, A, containing a vertical glass spiral, which was rotated at a constant rate by means of an electrically-driven motor such that the contents of the vessel were driven upwards into the gas phase and subsequently fell back into the pipette, a thorough mixing of the charge with the catalyst being obtained. The system was sealed against leakage of oxygen by a water jacket, B. The standard charge used for each test consisted of a constant amount of platinum, on a varied quantity of a given support, and 0·9 c.c. of 30% w/v hydrogen peroxide. The rate of evolution of oxygen at 20° and at atmospheric pressure was followed on the gas burette, C. The reaction was of first order, $k = (1/t)[\ln a/(a - x)]$, the symbols carrying their usual meanings, giving a linear graph on plotting log $[a/(a - x)]$ against time, t, and a slope of 0·0648 per min. The value of the constant, k, obtained was $1{\cdot}492 \times 10^{-1}$ per min. The measure of activity taken was the volume in c.c. of oxygen evolved in the first four minutes of the reaction, which does not affect the concentration of H_2O_2, and thus can be regarded as preliminary rates.

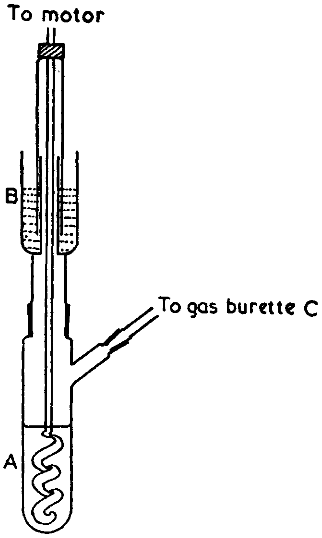

FIG. 1. The apparatus.

The relative activities of varying amounts of ThO_2, ZrO_2, Cr_2O_3, CeO_2, MgO, TiO_2, V_2O_5, and La_2O_3 have been separated, for clarity, into two Figures, Figs. 2 and 3, from

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[1] Lebedev and Trosman, *Zhur. fiz. Khim.*, 1960, **34**, 687.
[2] Maxted and Akhtar, *J.*, 1960, 1995.

which it will be seen that the activities at the peak points decrease in the sequence: $ThO_2 > ZrO_2 > Cr_2O_3 > CeO_2 > MgO > TiO_2 > V_2O_5 > La_2O_3 > Pr_6O_{11} > Tl_2O_3 > Sm_2O_3$. Further, in order to obtain a comparison with the activating effect of a widely used ordinary support, a curve with varying amounts of kieselguhr has also been included.

In order to separate the specific activating effect of these promoters from the influence of simple surface extension,[3] the relative surface areas of each of these supports was also determined by the B.E.T. method. These areas are given in Table 1, kieselguhr being included as a support since this probably has an activating effect dependent mainly on simple surface extension.

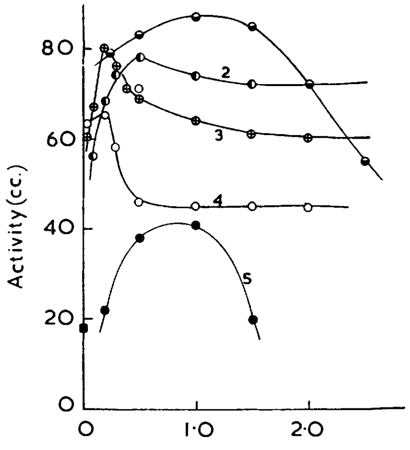

FIG. 2. The activity of platinum supported on: 1, thoria, 2, magnesium oxide, 3, ceria, 4, vanadium pentoxide, and 5, kieselguhr. The activity of unsupported platinum is shown at ■.

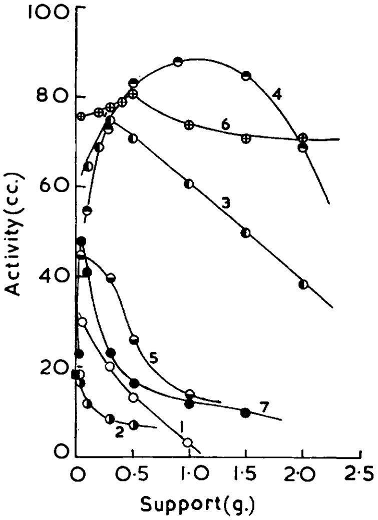

FIG. 3. The activity of platinum supported on: 1, thallic oxide, 2, samarium oxide, 3, titania, 4, zirconia, and 5, praseodymium sesquioxide, 6, chromia, and 7, lanthanum oxide.

TABLE 1.

Support	Total pore volume (ml./g.)	Amount of support corresponding to peak activity in g.	Surface area of support (m.^{2}/g.)	Surface area of support corresponding to peak activity (m.^{2}/g.)
ZrO_2	0·285	1·0	11·9	11·90
ThO_2	0·279	0·9	20·9	18·81
TiO_2	0·639	0·3	95·5	27·65
Cr_2O_3	0·364	0·5	45·6	22·80
MgO	0·608	0·5	24·2	12·10
V_2O_5	0·490	0·2	4·6	0·92
Kieselguhr	—	1·0	26·93	26·93

It will be seen from Figs. 2 and 3 that thoria and zirconia are by far the most effective supports used, in that the activity of the platinum was raised, at the peak point, from a value of about 18 for unsupported platinum to about 88 for thoria and to about 87 for zirconia, this being five times the original activity of the unsupported platinum, or more than twice the activity of the kieselguhr-supported platinum at its peak point.

The activation of two-component and three-component systems, made by precipitating platinum on physical mixtures of more than one oxide, was also studied. The activities

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

at the peak point of the two-component systems follow the sequence: $ThO_2 + ZrO_2 > CeO_2 + ThO_2 > Cr_2O_3 + ZrO_2 > Cr_2O_3 + ThO_2 > CeO_2 + ZrO_2$. The activation of platinum supported on the two-component system, $ThO_2 + ZrO_2$, is greater by about 10 on the scale than the activation of platinum on any of these oxides alone, the peak activity being about 98 when the zirconia content is as low as 10% in the system (Fig. 4). In the systems $Cr_2O_3 + ZrO_2$ and $CeO_2 + ThO_2$ the activities rise considerably in comparison with those of each of the oxides taken alone; but, in the systems $Cr_2O_3 + ThO_2$ and $CeO_2 + ZrO_2$ the activities first sink and then rise to the original value for each of the oxides used. This shows that the specific effect of these two combined promoters does not raise the activity to the same degree as that due to the two oxides used separately.

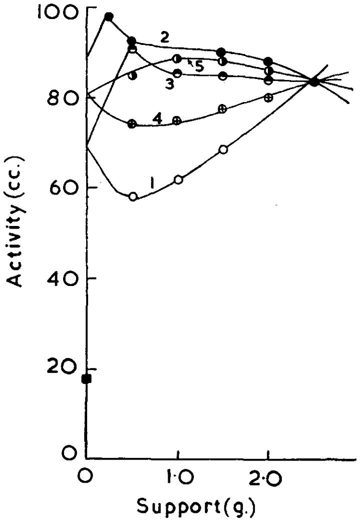

Fig. 4. The activity of two-component systems: 1, platinum on ceria with zirconia, 2, platinum on thoria with zirconia, 3, platinum on ceria with thoria, 4, platinum on chromia with thoria, and 5, platinum on chromia with zirconia.

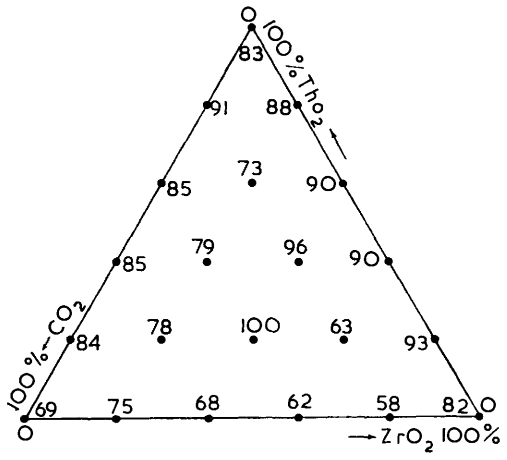

Fig. 5. The activity of platinum supported on three components: the three axes represent the three oxides used with increasing concentrations. Figures indicate the activity of the three components in c.c. of gas evolved in the first 4 min.

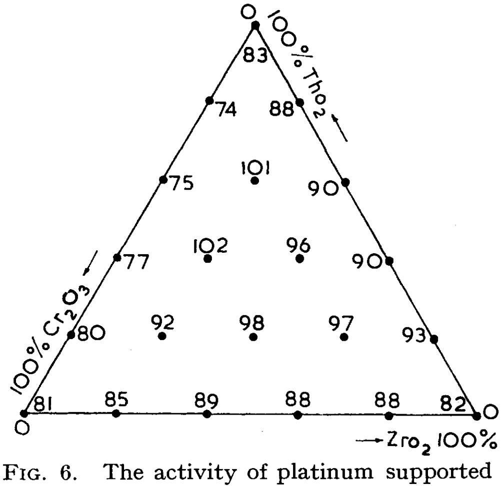

Fig. 6. The activity of platinum supported on three components: the three axes represent the three oxides used with increasing concentrations. Figures indicate the activity of the three components in c.c. of oxygen evolved in the first 4 min.

The supports studied in the three-component systems were thoria–zirconia–ceria and thoria–zirconia–chromium sesquioxide. Figs. 5 and 6 show, as three-dimensional triangular graphs, the activities of these two systems, the three co-ordinates being the ratios of the oxides to each other, and the numbers printed on the diagrams indicating the degree of activation obtained. Fig. 5 relates to the system zirconia–thoria–ceria and Fig. 6 to thoria–zirconia–chromium sesquioxide. The peak activation in the thoria–zirconia–ceria system is 100 when the ratio of thoria : zirconia : ceria is 20 : 40 : 40; and that of the thoria–zirconia–chromium sesquioxide system is 102 when the ratio of thoria : zirconia : chromium sesquioxide is 40 : 20 : 40. These three-component systems show in each case a definite, if not a great, rise in the activation effects if three supports are used in place of either one or two supports.

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