

Catalytic Decomposition of Hydrogen Peroxide on Platinum Supported Rare Earth Oxides

S.M. ISMAIL* AND KHURSHID A. KHAN**

Department of Chemistry, Al-Fateh University at Sebha, P.O. Box 18758 Sebha, Libya

(Received 17th September, 1980, Revised 25th March 1981)

Summary: Various authors¹⁻⁹ have used semi-conductors and insulators such as charcoal, silica gel and alumina gel as promoters for the decomposition of hydrogen peroxide by platinum catalysts. Walker et al¹⁰ have used glassy carbon as a support. In the present work, it was found that small quantities of rare earth oxides, cerium (IV) oxide, lanthanum (III) oxide, praseodymium (II) oxide, thallium (III) oxide and samarium (III) oxide act as strong promoters in the decomposition of aqueous hydrogen peroxide by finely divided platinum. The decomposition products were followed by a volumetric method. 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 the catalyst is further increased. The catalytic activities of these promoters follow the sequence: $\text{CeO}_2 > \text{La}_2\text{O}_3 > \text{Pr}_6\text{O}_{11} > \text{Tl}_2\text{O}_3 > \text{Sm}_2\text{O}_3$. The apparent activation energy of the decomposition of hydrogen peroxide in aqueous solutions have been determined at various temperatures. It is shown that there is a dependence of the activation energy on the temperature. A strict logarithmic dependence of the activation energy results in the disappearance of the promoter action of the supports at low temperatures. The surface of the oxides studied was thus shown to be irregularly heterogenous.

Introduction

The only approach to a complete understanding of a catalytic process is through an analysis of all factors involved, investigating each variable as completely separated from all other variables as possible. In molecular reactions the reactants must often be adsorbed to yield the product¹¹. The rate determining steps in such reactions may be the rate of adsorption or desorption of the reactants on the surface. By definition¹², catalysts reduce the activation energy of a reaction and thus an equilibrium is achieved through the formation of an activated complex with the catalyst. For supported catalyst in particular¹³, it is of interest to determine the separate contribution of the temperature independent factor¹⁴ and of the activation energy¹⁵ to the total activity, to know whether a support increases the activity by virtue of a decrease in the activation energy, by an increase in the frequency factor, or by both. Supported catalysts have been used to decompose hydrogen peroxide in aqueous solutions at temperatures considerably below inversion, in the region in which the reaction is strictly of the first order with respect to concentration. The rate determining steps have shown that the catalysts were

employed under conditions in which mass transfer did not control the reaction rates. For the first order reaction, if V = maximum volume of oxygen obtainable, v = volume obtained after time t , then the rate of reaction,

$\frac{dv}{dt} = k(V - v)$, where k is the rate constant. A plot of

$\log_{10} \frac{V}{V-v}$ against time t gave a straight line passing through the origin. The measure of activity taken was the concentration of H_2O_2 as titrated against 0.1M aqueous solution of potassium permanganate.

Experimental

All reagents used were of ordinary laboratory grade and were used as purchased. Potassium permanganate, being a primary standard, analytical reagent grade was used. Hydrogen peroxide (30% aqueous solution w/v) was obtained from Richard Harris. The concentration was determined by titration with 0.1M potassium permanganate (E. Mercke pro analysis) aqueous solution. Chloroplatinic acid was supplied by Johnson Matthey.

*To whom all correspondence should be addressed.

**Present address: Department of Chemistry, University of Gar Yunous Benghazi, Libya.

Preparation of the Catalysts

The catalysts were deposited on the supports by precipitation *in situ*. This method has been used with excellent results by the authors¹⁶. Finely divided platinum was prepared by the reduction of chloroplatinic acid with aqueous formaline. By this method, the tendency of platinum to form a sponge was avoided and the catalyst could then readily be separated by centrifuging. The rare earth oxides were sieved into 16-24 mesh and heated in air at 550° for 5 hours. The oxides were then immersed in 0.5M aqueous solution of chloroplatinic acid overnight. It was then reduced with formaline, centrifuged, dried and calcined in air at 600° for 5 hours. The metal contents of the supported catalysts were determined by atomic absorption spectroscopy.

Amount of Catalysts

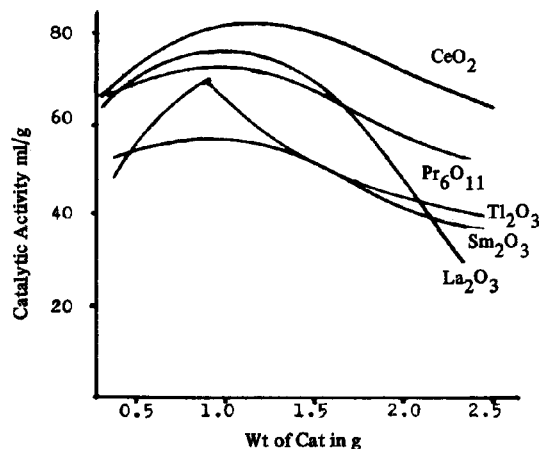
7.99 mg of reduced platinum was deposited on varying amounts, 0.1 to 2.0 g, of the rare earth oxides. The charge used for each test consisted of a constant amount of platinum (7.99 mg) on different amounts of rare earth oxide supports and 0.9 ml of 30% w/v hydrogen peroxide. With all consideration standardized at a constant, the dependence of the reaction rate upon the weight of the catalyst used was determined. This is shown in figure 1.

The Nature of the Catalysts

Under the same experimental conditions and with the same amount of the catalyst, the rate of decomposition of hydrogen peroxide over supported metallic oxides follow the sequence: $\text{CeO}_2 > \text{La}_2\text{O}_3 > \text{Pr}_6\text{O}_{11} > \text{Ti}_2\text{O}_3 > \text{Sm}_2\text{O}_3$. Blank experiments carried out with solutions containing no catalyst showed no oxygen evolution. The rate of reaction can be considered as preliminary rates as the evolution of oxygen was found to increase linearly with Pt^{4+} concentration. It is also a function of the amount of catalyst present and the rate of stirring, i.e. the efficiency of constant mixing between the catalyst and the solution.

Acitation Frequency

In a static system such as the present work, in which



1. Dependence of the reaction rate on the weight of the catalyst

the mixing of the solid and the liquid phases are carried out by shaking, it is important to ensure that the reaction rate is independent of the rate of shaking. The influence of the mode of frequency of agitation upon the rate of decomposition was determined for several different lots of catalysts using a magnetic stirrer at 920 rpm in comparison with a mechanical shaker operating at a frequency of 200 oscillations min^{-1} . The resulting data showed that the use of a mechanical shaker gave increased rates of decomposition for all weights of catalysts, and that this effect is more pronounced for some supports than for others. However, it was established after repeated experiments that the activity of 7.99 mg Pt on 1.0 g CeO_2 at 30° became independent of the rate of shaking when this exceeded 450 oscillations min^{-1} . As such, the shaking rates for all subsequent activity measurements were adopted at 550 oscillations min^{-1} , to take account of any variations due for instant, to belt slip.

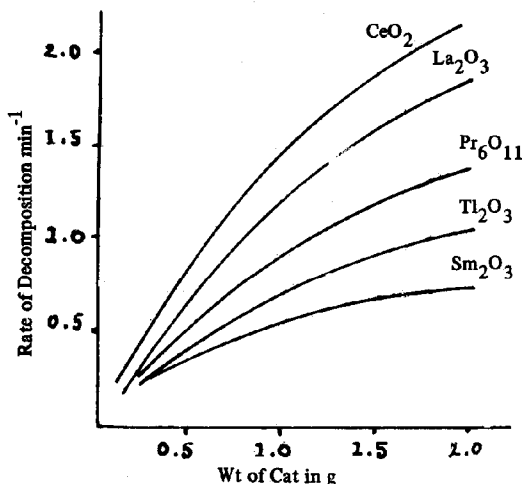
Procedure

The catalyst (0.1 – 2.0 g) was packed in a three neck reaction pipette (15mm i.d.). Two necks were used for the oxygen electrode and a glass tube for de-oxygenation, the third was connected to a gas impermeable system permitting samples of the solution to be taken out for analysis. The concentration of the catalyst Pt^{4+} could thus be checked continuously by absorbance measurements. A coefficient of $5.92 \times 10^3 \text{ mole}^{-1} \text{ ml}^{-1}$

was used throughout the calculations. H_2O_2 solution was fed from a reservoir at a rate of $7.15 \text{ ml}^3 \text{ min}^{-1}$ by a roller pump. The concentration of H_2O_2 at the outlet of the catalyst column was determined by titration with $KMnO_4$. The outflow was frozen with liquid nitrogen and its UV-spectrum was measured. UV-spectra was recorded on a Pye-Unicam UV-visible SP 8-100 Spectrophotometer.

Results and Discussion

The rate of decomposition of H_2O_2 over supported oxides was determined by measuring the conversion as a function of constant time (Figure 2). In all cases, the decomposition was found to be of the first order with respect to the concentration of H_2O_2 . The rate constant is expressed as k_1 in the unit of per mole of the supported metal. The pH dependence of the rate constant was determined over a wider range for the decomposition of H_2O_2 with supported Pt (Figure 3). The value of k_1 increases with increasing pH upto 9 and is level between pH 9 and 10, and decreases with further increase in pH. The kinetic behaviour of supported Pt indicates that the oxidation states of metals of the starting material is not decisive in determining the catalytic activity for H_2O_2 decomposition and that there exists a reduction-oxidation equilibrium between variable oxidation states during the reaction. This suggests that there exists a reduction-oxidation interconversion of the variable valence states of the metallic cations during the reaction. The values of the rate constant increase with increase in the



2. Dependence of the reaction rate on time.

oxidation potential, reach a maximum and decrease with further increase in the oxidation potential.

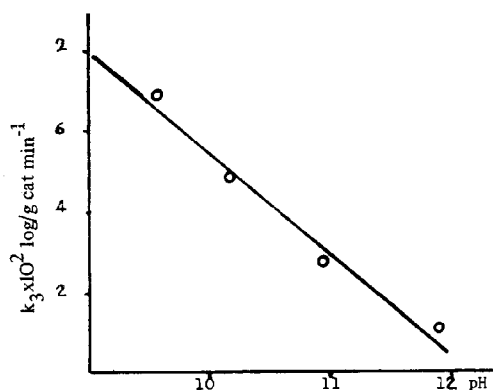
Kinetic Factors

The first order dependence of the reaction rate on the weight of the catalyst is a necessary condition for the absence of mass transfer effects. As the amount of the catalyst is increased, the reaction rate increases linearly at first, but subsequently becomes independent of the weight of the catalyst. Watt and Willing¹⁸ represented this limiting value by an empirical formula: $k = Awp / (1 + Bw)$, where w is the weight of the catalyst, k the reaction rate, p the pressure and A, B are constants. The activities of increasing amounts of platinum on cerium (IV) oxide at 30° do not deviate from linearity until more than 1 g of platinum was employed. Accordingly, the small amounts of catalysts which were used subsequently (0.1 to 2.0 g supports and 7.99 mg Pt) were well within range of linear dependence of the activity on the weight of the catalyst.

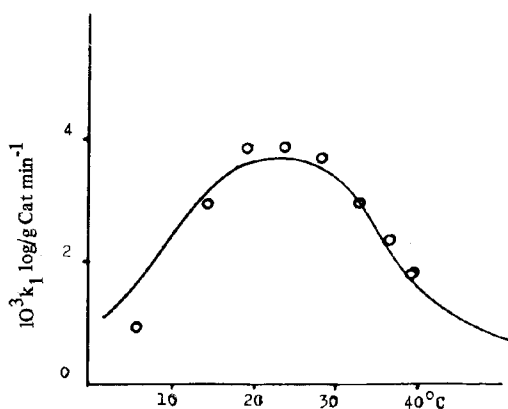
The rate of decomposition of H_2O_2 for each support was determined between 0° and 40° ; the temperature was thermostatically controlled within $\pm 0.2^\circ$. This is shown in Figure 4. It was necessary to correct the rates for the partial pressure of water, since the rate at a given pressure is proportional to the partial pressure of oxygen¹⁷⁻²⁰. The validity of this correction has already been shown²²⁻²³.

The rate of decomposition of H_2O_2 at unit pressure, i.e. the specific reaction rate can be expressed by the relationship: $k_1 = wSk_s$, where w is the weight of Pt, S its specific surface area and k_s the activity per unit area. The activity is related to a frequency factor A , and the apparent energy of activation E_A , by the Arrhenius expression $k_s = A \exp(-\frac{E_A}{RT})$. From the standpoint of collision theory, A may be equated to the collision number Z and a steric factor P . Plots of $\log k_1/wc_0$ against $1/T$ are given in Figure 5 for different ratios of Pt on supports containing the optimal ratio of Pt/support activity at maximum.

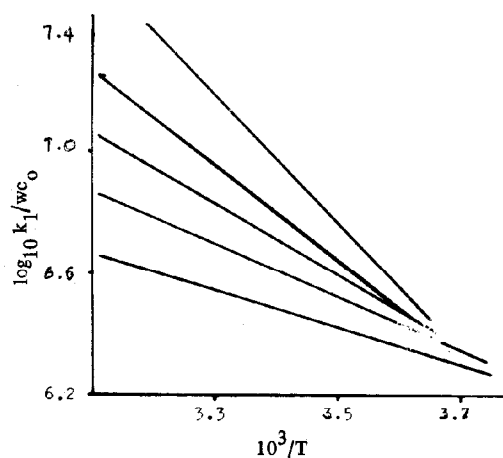
If k is the true velocity constant, K_H the adsorption coefficient of oxygen in the Langmuir-Rideal mechanism²⁴ and p_H the partial pressure of oxygen, the reaction rate is given by $v = kK_H p_H$ and the true first order velocity constant $k_1 = kK_H$. It can readily be shown that whenever the apparent first order constant is given by the product of an adsorption equilibrium constant and



3. Rate of reaction against pH.



4. Dependence of the reaction rate on temperature.

5. Plots of $\log_{10} k_1/wc_0$ against $1/T$.

the true velocity constant, the apparent activation energy is lower than the true activation energy by the value of the heat of desorption of oxygen, irrespective of the reaction mechanism. The apparent activation energies should therefore be corrected by the addition of 16-18 kcal mole⁻¹ in order to obtain the true values.

Another factor which can affect the activation energy observed, for a series of related catalysts, is a compensation effect between the activation energy and the frequency factor. The absence of a strict logarithmic relation between E_A and A is apparent in Figure 4, since a necessary condition for this is that Arrhenius plots should intersect at a common point, i.e. a temperature exists at which all the reaction rates are equal. Nevertheless, it is evident that the relative activities at a given temperature also depend on the activation energy.

At room temperature, promoter action of the supports becomes active, since the specific activities of the supported catalysts are greater than the corresponding activity of unsupported platinum. Owing to a compensation effect, the degree of this promoter action becomes smaller as the temperature decreases. At sufficiently low temperatures, the increase in the temperature independent factor for the supported catalysts becomes inadequate to overcome the effect of a larger activation energy, and promotion does not occur. For supported catalysts, these temperatures lie in the experimental region between 3^o and 15^o.

The temperature coefficient of the catalytic processes is also of considerable importance. By virtue of the dependence of the reaction velocity on the absorbed concentration, the decrease in the velocity as the temperature is increased, may occur at high temperatures. A change in the kinetic form with increasing temperatures has been observed. For this reason, the reaction temperature was kept as low as possible, an optimum being found to be at 30^o.

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