Decomposition of Aqueous Hydrogen Peroxide Over Chromic Oxide Catalysts

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Chromia and chromia–alumina catalysts contain excess surface oxygen after oxidation at 500°.[1–3] The extent of surface oxidation has been found to be qualitatively related to the activity for the catalytic decomposition of aqueous hydrogen peroxide. Figure 1 shows the results obtained for both oxidized and reduced samples of the three catalysts tested, *i.e.*, stabilized chromia gel, 20% chromia impregnated on alumina (Houdry Type R catalyst), and coprecipitated chromia–alumina (35% Cr_2O_3). The reaction rates were determined from the slopes of the curves obtained by plotting oxygen liberated *vs.* time. In most of the runs these curves were straight lines, but in several runs with the chromia–alumina catalysts the reaction rate increased, and the aqueous phase turned purple, after several hundred seconds. In these few cases the slopes of the initial straight portions of the curves were used. The oxidized catalysts are 6–8 times more active than the reduced ones.

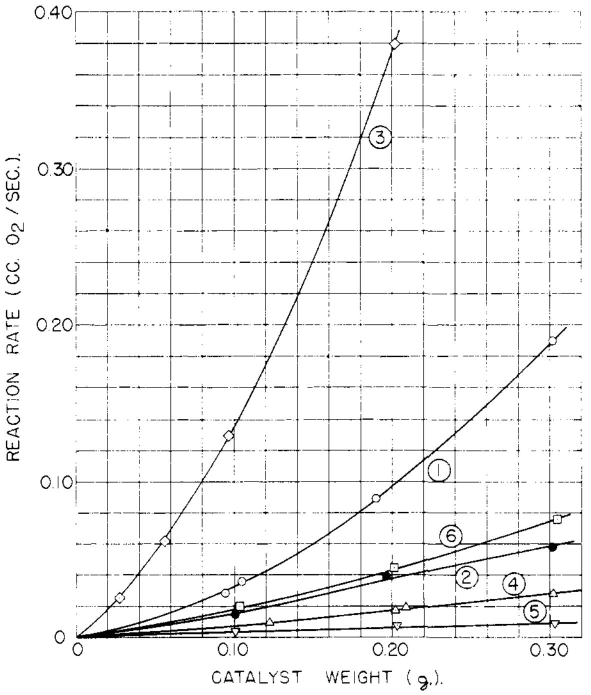

Fig. 1.—Catalytic decomposition of aqueous hydrogen peroxide at 30°: (1) oxidized Cr_2O_3; (2) oxidized Cr_2O_3–Al_2O_3 (Houdry Type R); (3) oxidized coppt. Cr_2O_3–Al_2O_3; (4) reduced Cr_2O_3; (5) reduced Cr_2O_3–Al_2O_3 (Houdry Type R); (6) reduced coppt. Cr_2O_3–Al_2O_3.

The extent of surface oxidation (expressed as equivalent CrO_3), the titratable acidity, and the *p*H of the aqueous suspension of each catalyst are given in Table I. In the case of the chromia gel there is a direct relationship between the surface oxidation and the catalyst acidity as determined by the *p*H measurement. The oxidized catalyst contains the equivalent of 1.9% CrO_3; an aqueous suspension of 100 g. of catalyst per liter would, therefore, be expected to have a *p*H corresponding to a chromic anhydride concentration of 1.9 g. per liter. The *p*H values of a number of pure chromic anhydride solutions were determined and from these data the *p*H of one containing 1.9 g. of CrO_3 per liter was found to be 2.7–2.8. The experimentally determined *p*H for the oxidized chromia gel is 2.71 (Table I). The reduced chromia gel contains no excess surface oxygen, and its aqueous suspension is, correspondingly, almost neutral.

TABLE I

CATALYST CHARACTERISTICS

Catalysts	Oxidation (CrO_3, %)	Titratable acidity (meq./g.)	*p*H of aqueous suspension
Oxidized chromia gel	1.9	0.173	2.71
Reduced chromia gel	<0.1	.048	6.67
Oxidized chromia–alumina (Houdry Type R)	1.8	.146	6.20
Reduced chromia–alumina (Houdry Type R)	<0.2	.016	9.44
Oxidized coppt. chromia–alumina	9.6	.72	5.10
Reduced coppt. chromia–alumina	<0.2	.00	9.68

This type of calculation cannot be simply made for the chromia–alumina catalysts as the presence of the alumina affects the *p*H. It should be noted, however, that even in the presence of the alumina, the surface oxidation and the *p*H values are in qualitative agreement.

The titratable acidities are also in qualitative agreement with the surface oxidation and *p*H measurements. Complete quantitative agreement could probably be established, if a correction were made for the error in the determination of the end-point in the acid-base titration. Phenolphthalein was used as the indicator in this method; since the *p*H change at the end-point is not sharp, the indicator end-point does not correspond to the exact equivalence point.

X-Ray diffraction patterns and other evidence[3] indicate that oxidation of these catalysts at 500° is limited to the surface. The oxygen represented by the 1.9% CrO_3 in oxidized chromia gel, which has a surface area of 35 $m.^2/g.$, corresponds to about one-third of a monolayer of close-packed oxide ions on the surface. The amount of excess oxygen contained by the chromia–alumina catalysts also corresponds to less than a monolayer.

In order to show that the catalytic activities of the oxidized catalysts depend on the amounts of surface oxidation, a comparison was made with pure chromic anhydride; the results are shown in Table II. Column 2 gives the weight of oxidized catalyst used in each catalyst test, and column 3 shows the corresponding amounts of excess surface oxygen, expressed as chromic anhydride, computed from the data of Table I to be present on the cat-

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(1) G. N. Maslyanskii and N. R. Bursian, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 208 (1948).

(2) J. Givaudon, E. Nagelstein and R. Leygonie, *J. chim. phys.*, **47**, 304 (1950).

(3) S. Voltz and S. Weller, unpublished work.

alyst. Column 4 shows the amount of pure chromic anhydride which was found experimentally to have the same (initial) activity for aqueous peroxide decomposition as did the given weight of catalyst. The approximate correspondence between the values in columns 3 and 4 indicates that the activities of the oxidized catalysts for this reaction can be largely attributed to the chromic anhydride, or its equivalent, formed on the surfaces of these catalysts during high temperature oxidation.

TABLE II

COMPARISON OF SURFACE OXIDATION AND CHROMIC ANHYDRIDE REQUIRED FOR THE SAME REACTION RATE

(1) Catalyst	(2) Wt. cat., g.	(3) CrO_3 present in cat., mg.	(4) Pure CrO_3 required for same activity, mg.
Oxidized chromia gel	0.10	1.9	4
Oxidized chromia gel	.20	3.8	9
Oxidized chromia gel	.30	5.7	11
Oxidized chromia–alumina (Houdry Type R)	.10	1.8	2
Oxidized chromia–alumina (Houdry Type R)	.20	3.6	4
Oxidized chromia–alumina (Houdry Type R)	.30	5.4	7
Oxidized coppt. chromia–alumina	.05	4.8	6
Oxidized coppt. chromia–alumina	.10	9.6	9
Oxidized coppt. chromia–alumina	.20	19	14

The finite activity of the reduced samples, in spite of their negligible CrO_3 content, is responsible for the fact that the ratio of activities of the oxidized to the reduced samples is less than the ratio of the CrO_3 contents of the same samples.

Experimental

The chromia gel was prepared from dilute solutions of ammonium hydroxide and chromium nitrate, dried in air at 110°, and then stabilized by several cycles of oxygen and hydrogen at 500° (ending with oxygen). The 20% chromia–alumina impregnated catalyst is the Houdry Type R catalyst, which is used for the commercial production of butadiene. The coprecipitated chromia–alumina catalyst was prepared from solutions of sodium aluminate (80 mole per cent.) and chromium acetate (20 mole per cent.) and dried in air at 110° and finally at 500°.[4,5]

The surface areas of the stabilized chromia gel and the 20% chromia–alumina (Houdry Type R) are 35 and 50 m.^{2}/g., respectively. Coprecipitated chromia–alumina catalysts of the type used in this work have areas several times greater than these.

Each catalyst was pretreated with oxygen or hydrogen at 500° in a flow system and after being cooled in the pretreatment gas to 30° was transferred to a static system. Five cc. of 30% hydrogen peroxide were then added to the catalyst and the rate of reaction determined by measuring the amount of oxygen liberated as a function of time.

When the reaction rate was slow, the liberation of oxygen was followed for about ten minutes. With the more active catalysts the reaction was followed until the liberation of about 50 cc. of oxygen.

The extent of surface oxidation was determined by an iodometric method.[1–3] The titratable acidity was determined by adding standard sodium hydroxide to a weighed amount of catalyst and then, after a given time, titrating with standard hydrochloric acid; the acidity values given in Table I are the extrapolated values at zero time. The *p*H values were determined by suspending 1 g. of catalyst in 10 cc. of distilled water and vigorously stirring the suspension for several hours until a constant *p*H was obtained.

Powdered catalysts were used in all the experimental work reported in this note.

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[4] E. Buck and E. C. Hughes, U. S. Patent 2,290,033, July 14, 1942.

[5] E. C. Hughes, U. S. Patent 2,323,868, July 6, 1943.

Temperature Coefficient of the Radiation Induced Oxidation of Ferrous Sulfate[1]

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Three determinations of the temperature coefficient of the radiation induced oxidation of air-saturated ferrous sulfate solutions have appeared. Dewhurst[2] found a coefficient of 0.4% per degree, Hardwick[3] found 0.2% per degree and Minder and Liechte[4] found no dependence but did not state their limits of error.

In the mechanism that is accepted for this reaction[5] the hydrogen atoms, hydroxyl radicals and hydrogen peroxide produced react stoichiometrically with the ferrous ions with no competing steps. Hence any temperature coefficient found should represent a change in the net dissociation of the water.

Experimental

Triply distilled water was used in preparing the solutions.[6] The solutions were 0.001 *M* in ferrous sulfate and sodium chloride (to inhibit any organic effect[7]) and 0.8 *N* in sulfuric acid. All equipment used was cleaned with steam. The irradiation cells were preirradiated with several million roentgen. A water thermostated cylindrical cobalt-60 source[8] was used in the irradiations. All results were corrected to the same time on the basis of a 5.2 year half-life of the source.

Ferric ion was determined spectrophotometrically by direct reading of the absorption of the ferric sulfate complex at 305 mμ on a Beckman DU spectrophotometer,[9] using an extinction coefficient of 2190. Since all optical density measurements were made at room temperature, the effect of change in density of the solution cancels out.

Suitable thermal controls were run with the samples, a portion of the ferrous sulfate solution being kept at the reaction temperature during the irradiation. The amount of oxidation in the blanks was very small, amounting to only 1% of the observed radiation induced reaction at 72°.

Discussion

The results for solutions with chloride ion added are given in Fig. 1. Each point is an average of between 4 and 8 determinations. The temperature coefficient found is 0.04 ± 0.03% per degree,

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] H. A. Dewhurst, doctoral dissertation, McGill University, Montreal, Que. (1949).

[3] T. J. Hardwick, *Can. J. Chem.*, **31**, 881 (1953).

[4] N. Minder and A. Liechte, *Experientia*, **2**, 410 (1946); see also C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

[5] F. H. Krenz and H. A. Dewhurst, *ibid.*, **17**, 1337 (1949).

[6] E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

[7] H. A. Dewhurst, *J. Chem. Phys.*, **19**, 1329 (1951).

[8] H. A. Schwarz and A. O. Allen, *Nucleonics*, in press.

[9] T. J. Hardwick, *Can. J. Chem.*, **30**, 17 (1952).