

Decomposition of Dilute Hydrogen Peroxide in Alkaline Solutions

In the development of an oxygen electrode for electrochemical fuel cells, it has been of interest to find effective catalysts for the decomposition of hydrogen peroxide in aqueous solutions of potassium carbonate and potassium hydroxide. We have compared the activity of fourteen catalytic solids.

The following apparatus and experimental procedure were developed for this investigation: a 200-ml. three-necked distilling flask was used as the reactor. The centre neck contained a glass rod from a variable-speed motor which drove a 'Teflon' stirrer blade at 210 r.p.m. The shaft was sealed in a gas-tight sleeve and marked for stroboscopic measurement of rotation speed. One side-neck was connected to a eudiometer which had a levelling bulb filled with the same solution as the reactor. The eudiometer served to maintain the reactor at atmospheric pressure.

The other side-neck contained the charging device, which was a glass tube held in place with a rubber stopper. The glass tube contained the weighed charge of catalyst held between two 'Teflon' plugs. A 12-in rubber tube, the centre of which held a stainless steel rod, was connected to the charger tube; the charging unit was made gas tight by sealing the free end of the rubber tube. The steel rod was used to force the charge (catalyst and 'Teflon' plugs) from the glass tube into the stirred reactor solution.

'Baker Analysed' reagent grade hydrogen peroxide without preservative was used to prepare the hydrogen peroxide solution. Titrimetric determinations were made with standardized potassium permanganate solution before each run. The reactor was filled with 50 ml. of 6.90 M potassium hydroxide or 4.09 M potassium carbonate to which 5 ml. of the standardized 1.0 M hydrogen peroxide was added with a hypodermic syringe. The catalyst charger was then attached to the reactor, and the stirring motor started. After adjustment of the liquid-levels with the levelling bulb, the timer was started and the catalyst released. The volume of gas evolved was recorded as a function of time.

Blank runs were made by injecting the two 'Teflon' holding plugs, without catalyst, into the reactor and observing the rate of oxygen evolution. The blank run in potassium carbonate solution showed negligible oxygen evolution. In potassium hydroxide solution the determined blank rate of oxygen evolution was 1.2×10^{-3} ml./sec.

Table 1. A COMPARISON OF CATALYTIC ACTIVITY OF VARIOUS SOLID CATALYSTS IN THE DECOMPOSITION OF 0.09 M HYDROGEN PEROXIDE AT 22° C IN AQUEOUS SOLUTIONS OF 0.9 M POTASSIUM HYDROXIDE AND 4.1 M POTASSIUM CARBONATE

Catalyst powder	Source	Rate $\left(\frac{\text{ml.} \times 100}{\text{g sec}}\right)$		Surface area (m ² /g)
		0.9 M KOH	4.1 M K ₂ CO ₃	
Ag ₂ O	Ames Lot No. 932	887.0	1,410.0	0.348
Platinum black	Ref. 2	810.0	1,065.0	14.7
Unsymmetrical cobalt ferrite	Co _{1.1} Fe _{0.4} O ₄ , LMSC	287.0	482.0	16.8
Raney silver	Raney Catalyst Co.	274.0	98.0	3.36
Palladium black	Ref. 3	267.0	770.0	7.60
Precipitated silver	Fisher certified reagent	170.0	88.0	0.13
'Darco G-60' carbon	L. H. Butcher Co.	18.6	33.0	461.0
MnO ₂	Mallinckrodt Lot No. 6133	9.4	26.0	0.345
Co ₂ O ₃	J. T. Baker Lot No. 2249	8.3	34.0	2.66
Fe ₂ O ₃	J. T. Baker Reagent	5.7	6.3	7.25
Gold	Englehard 100 mesh	3.3	6.1	0.1
Nickel black	Ref. 4	3.25	4.7	8.50
Unsymmetrical nickel ferrite	Ni _{1.02} Fe _{0.44} O ₄ , LMSC	2.8	1.8	0.789
Symmetrical nickel ferrite	Ni ₁ Fe ₂ O ₄ , LMSC	1.6	1.8	0.647

Surface area measurements¹ had a precision of 5 per cent and accuracy was checked against standardized samples purchased from the Stanford Research Institute, Menlo Park, California.

In the evaluation of the collected data, it was found that the initial rate of reaction, expressed in volume (at s.t.p.) per unit time per unit weight of per unit area of catalyst, gives a quantitative and reproducible measure of catalyst activity. Initial rates were obtained by extrapolation of the volume-time data to time equal to zero. The values in Table 1 give the initial activities of the 14 tested catalysts. Each value is the averaged value of three runs; the average deviation is less than 5 per cent.

Silver oxide was found to be the most active catalyst in both solutions. Platinum black, unsymmetrical cobalt ferrite, and palladium black also promoted the rapid decomposition of hydrogen peroxide under the conditions of the experiment. The first six catalysts listed in Table 1 have marked activity in catalysing hydrogen peroxide decomposition. Activity was generally higher in the potassium carbonate solution than in the potassium hydroxide solution; the three exceptions were Raney silver, precipitated silver, and unsymmetrical nickel ferrite. In practice, the use of a catalyst that ensures a low peroxide activity results in increased electrode performance.

The experimental method also permits the measurement and comparison of specific rates (rates per unit area). These specific rates are useful in indicating potential activity by considering them together with the maximum attainable surface area per unit weight or catalyst. For example, carbon with a relatively low specific rate may be prepared in forms which are moderately active because of their high surface area (Table 1). Gold was found to

have a very high specific rate, and the collected results led to the conclusion that gold catalysts prepared with high surface areas should be very effective in peroxide decomposition.

This experimental technique can encounter at least two difficulties. Gas pockets formed in the dried solid catalyst may act to mask a certain fraction of the reaction sites, and fine particles of catalyst may tend to agglomerate so that they are difficult to disperse.

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¹ Barr, W. E., Anhorn, V. J., and Joyner, L. G., *Scientific and Industrial Glass Blowing*, 257 (Instruments Pub. Co., Pittsburgh, 1959).

² Loew, O., *Ber.*, 23, 289 (1890).

³ Mond, L., *et al.*, *Trans. Roy. Soc.*, A, 191, 106 (1898).

⁴ Berezina, S. J., *et al.*, *Doklady Akad. Nauk S.S.S.R.*, 77, 53 (1951).