

# CATALYTIC PROPERTIES OF $\text{Al}_2\text{O}_3\text{-ZrO}_2$ AND $\text{Al}_2\text{O}_3\text{-TiO}_2$ BINARY OXIDE CATALYSTS FOR DECOMPOSITION OF $\text{H}_2\text{O}_2$

by S. P. WALVEKAR and A. B. HALGERI, *Department of Chemistry, Central College, Bangalore University, Bangalore-560001*

(Communicated by Prof. S. K. Bhattacharyya, F.N.A.)

(Received 1 August 1973)

The decomposition of  $\text{H}_2\text{O}_2$  in the presence of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  and  $\text{Al}_2\text{O}_3\text{-TiO}_2$  mixed oxide catalysts (ignited to various temperatures) has been studied. As these catalysts are of bifunctional nature, an attempt has been made to evaluate the decomposition brought about by acidic as well as by the basic sites by the poisoning technique. The results indicate that both these sites catalyse the decomposition of  $\text{H}_2\text{O}_2$  and the decomposition is directly proportional to the acidity and basicity of the catalyst. The energy of activation values  $E_a$  and  $E_b$  are inversely proportional to the acidity and basicity values.

## INTRODUCTION

The decomposition of  $\text{H}_2\text{O}_2$  occurs readily on numerous solid surfaces in aqueous solution at close to room temperatures. Therefore, it is very convenient for the purpose of evaluation of catalytic properties and prediction for catalyst selection based on catalytic properties. The catalytic decomposition of  $\text{H}_2\text{O}_2$  in presence of oxides and mixed oxides has been investigated by several workers (Krause 1965; Deren & Haber 1965; and Chopra *et al.* 1970). Very little work has been done on the nature of catalyst surface by the poisoning technique; hence the present work is initiated to throw more light on the nature of the catalyst surface and the decomposition of hydrogen peroxide.

An attempt has been made to evaluate the amount of decomposition of  $\text{H}_2\text{O}_2$  brought about by the acidic sites as well as by the basic sites by the poisoning technique and also correlate these with the acidity, basicity and the energy of activation calculated from the kinetic data at different temperatures.

## EXPERIMENTAL

*Reagents* : Merck's quality  $\text{H}_2\text{O}_2$  was purified by distillation at reduced pressure and was used. All the other chemicals used in the investigation were of AnalaR quality.

*Catalyst preparation* : Alumina-zirconia and alumina-titania were prepared by the coprecipitation technique (Nicolescu & Chiok 1969). The mixtures of the precipitated hydroxides were digested for several hours and then filtered, washed and dried at  $120^\circ\text{C}$  for 20 hours. The samples thus obtained were powdered and only such of the samples as were collected between 100 and 150 mesh sieves were used. The powders were subjected to heat treatment in the temperature range  $120^\circ\text{C}$  to  $1000^\circ\text{C}$ , by heating the sample to the desired temperature for six hours in an electric

muffle furnace with temperature control arrangement. The samples after heat treatment were cooled in a desiccator and preserved in covered glass tubes, under vacuum.

*Measurement of surface acidity and basicity* : The acidity of these mixed oxides was measured by amine titration method (cf. Johnson 1955) using *p*-dimethyl aminoazobenzene ( $pK_a = +3.3$ ) and dicinnamal acetone ( $pK_a = -3.0$ ) as indicators. The surface basicity of these catalysts has been measured by the phenol adsorption method in benzene solution (Halgeri 1972).

*Kinetic studies* : 100 ml of 0.012M~ 0.2M solution of hydrogen peroxide in double distilled water and 1.0 g of mixed-oxide catalyst were kept in flasks maintained at 30°C and 40°C, in a thermostat. The  $H_2O_2$  underwent decomposition in the presence of the acidic and basic centres on the surface of the catalyst. The amount of  $H_2O_2$  that decomposed was estimated by titrating the undecomposed  $H_2O_2$  against 0.02M  $KMnO_4$  solution at regular intervals of time.

Experiments were carried out with different samples of the catalyst that had been ignited for 6 hours at different temperatures in the range 120°C to 1000°C.

Since the present catalysts have both acidic as well as basic sites on their surface and that both these sites catalyse the decomposition of  $H_2O_2$ , an attempt has been made to evaluate the amount of decomposition brought about by the acidic as well as the basic centres. For this purpose the acidic sites were poisoned by neutral red ( $pK_a = +6.8$ ) and the catalyst used to evaluate the decomposition by basic centres on the catalyst surface and similarly the basic centres were poisoned by HCl and the catalyst used to evaluate the decomposition by acidic centres on the catalyst surface. Neutral red and HCl were selected for the purpose of poisoning the acidic and the basic sites on the surface of the catalyst as these were found to have no effect on the decomposition of  $H_2O_2$ .

Since the decomposition of  $H_2O_2$  is a very sensitive reaction (cf. Grossner *et al.* 1971) the catalyst samples used were those which had the same acidic and basic properties throughout and were tested for their acidic and basic properties before the start of every decomposition reaction.

## RESULTS AND DISCUSSION

The values of the acidities presented in Tables I and II, were measured at  $pK_a = +3.3$ . For evaluating this value, the total value of acidity at  $pK_a \leq +3.3$  and also at  $pK_a \leq -3.0$  were measured by amine titration method (Cf. Johnson 1955). The difference of these two values gave the acidity at nearly  $pK_a = +3.3$ . This eliminates the effect of water, which has a  $pK_a = -1.7$ , i.e., a mild base which has been found to neutralise all acid sites having a  $pK_a \leq -3.0$  (Matsuzaki & Fukuda 1970) and hence, all strong acidic sites which are not neutralised by water, i.e., with  $pK_a \leq +3.3$  will bring about the decomposition of  $H_2O_2$ .

The values of  $K$  (the rate constant for the catalyst as a whole),  $K_a$  and  $K_b$  (rate constants for the acidic and basic sites) were calculated from the slopes of the rate curves,  $\log(a-x)$  against time ' $t$ ', which were straight lines. These values are presented in Tables I and II.

The plots of  $K_a$  against acidity and  $K_b$  against basicity (Fig. 1, 2) are straight lines which implies (Walvekar & Halgeri 1973) that both acidic and basic

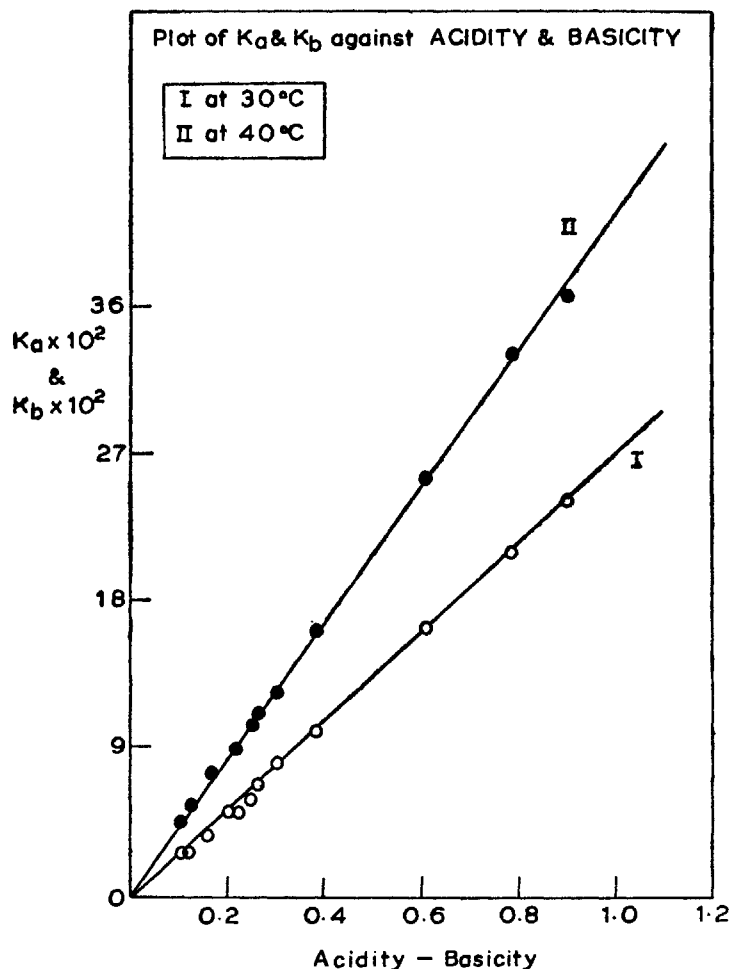


FIG. 1. The dependence of catalytic activity for decomposition of  $H_2O_2$  on the number of acidic and basic centres of alumina-zirconia catalyst.

sites bring about decomposition of  $H_2O_2$ . The sum of  $K_a$  and  $K_b$  is nearly equal to  $K$  in all cases. These results indicate that the contribution of the acidic and basic sites is nearly the same in terms of decomposition of  $H_2O_2$  per mole of acidic or basic sites. The relative rate constant values for  $Al_2O_3-ZrO_2$  are greater than those of  $Al_2O_3-TiO_2$  obviously for the reason that the  $Al_2O_3-ZrO_2$  has large number of acidic and basic sites than the corresponding  $Al_2O_3-TiO_2$  catalyst. It is also observed that  $E_a$  and  $E_b$  are inversely proportional to the acidity and basicity respectively (Tables I and II). This observation is in agreement with the accepted theories and also with the observation made by Fischer and Sebba (1961) in the decomposition of formic acid over  $SiO_2-Al_2O_3$  catalyst. From these results it can be concluded that the mechanism of decomposition of  $H_2O_2$  by acidic and basic sites is nearly of

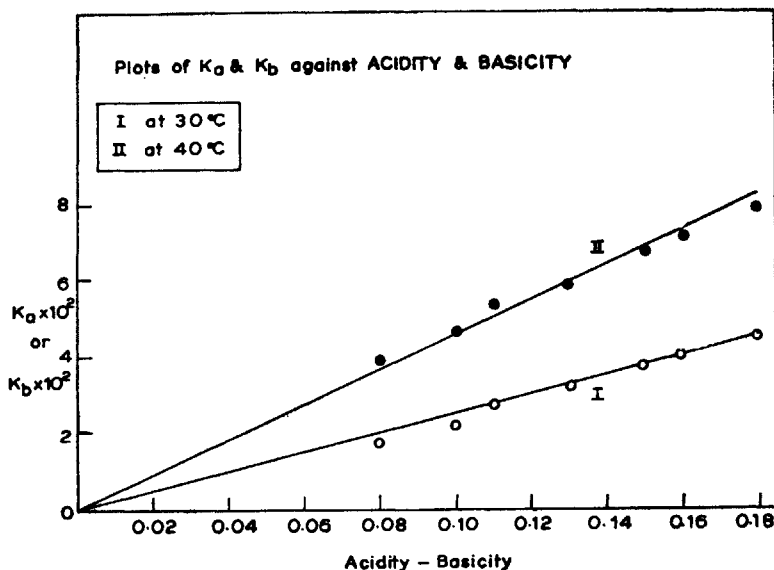


FIG. 2. The dependence of catalytic activity for decomposition of  $H_2O_2$  on the number of acidic and basic centres of alumina-titania catalyst.

TABLE I

*Decomposition of  $H_2O_2$  in presence of Alumina-Zirconia (80%—20%) catalyst*

Sl. No.	Tem- perature of ignition °C	Acidity mmoles/g pKa=3.3	Basicity mmoles/g	Rate constant $hr^{-1}g^{-1}$				$E_a$ calories per mole	$E_b$ calories per mole		
				$K \times 10^2$ at 30°C	$K_a \times 10^2$ at 40°C	$K_b \times 10^2$ at 30°C	$K_b \times 10^2$ at 40°C				
1	120	0.12	0.90	28.5	43.2	2.6	5.1	24.0	36.5	13830	7943
2	260	0.20	0.78	26.0	43.0	5.0	9.0	21.0	33.0	11130	8565
3	380	0.25	0.60	21.0	37.0	5.7	10.5	16.1	25.5	11570	8734
4	500	0.30	0.38	20.0	30.0	8.2	12.5	10.0	16.1	7987	9022
5	610	0.22	0.26	12.0	21.0	5.0	9.0	6.9	11.2	11130	9349
6	720	0.16	0.20	8.4	17.0	3.7	7.5	4.8	9.0	13390	11910
7	800	0.10	0.10	5.1	10.0	2.3	4.8	2.6	5.2	13940	13130
8	1000	—	—	—	—	No reaction		—	—	—	—

the same nature. It is further concluded that in case of  $Al_2O_3 - ZrO_2$  and  $Al_2O_3 - TiO_2$  catalysts which are of bifunctional nature, the decomposition of  $H_2O_2$  is directly proportional to the acidity and basicity of the catalyst.

Experiments were tried with different concentrations of  $H_2O_2$  keeping the quantity of the catalyst the same. It is seen from Table III that the values of  $K$  are nearly constant for each of the catalysts indicating that change of the concentration of

TABLE II

*Decomposition of  $H_2O_2$  in presence of Alumina-titania (74%—26%) catalyst*

Sl. No.	Temperature of ignition °C	Acidity mmoles/g pKa = 3.3	Basicity mmoles/g	Rate constant $hr^{-1}g^{-1}$					$E_a$ calories per mole	$E_b$ calories per mole	
				$K \times 10^2$ at 30-C	$K \times 10^2$ at 40-C	$K \times 10^2$ at 30-C	$K \times 10^2$ at 40-C	$K \times 10^2$ at 30-C			$K \times 10^2$ at 40-C
1	120	0.08	0.18	7.2	14.4	1.8	4.1	4.5	7.9	15600	10660
2	220	0.10	0.16	6.5	13.0	2.3	4.9	4.1	7.2	14320	10670
3	320	0.10	0.15	5.8	12.1	2.2	4.7	3.8	6.8	14380	11030
4	420	0.10	0.13	5.1	11.8	2.2	4.8	3.2	6.0	14780	11910
5	500	0.08	0.13	5.0	11.2	1.8	4.0	3.1	5.9	15130	12190
6	600	0.08	0.11	4.2	10.1	1.7	3.9	2.8	5.4	15730	12440
7	700	—	—	No reaction takes place							
8	800	—	—	—do—							
9	1050	—	—	—do—							

TABLE III

*Rate constants at 30°C for the  $H_2O_2$  decomposition at various concentrations of  $H_2O_2$* 

Concentration of $H_2O_2$ moles/l.	Rate constant ( $K \times 10^2 hr^{-1} g^{-1}$ ) for catalysts	
	$Al_2O_3-ZrO_2$ (500°C)	$Al_2O_3-TiO_2$ (200°C)
0.012	20.04	6.52
0.062	21.28	6.94
0.086	21.54	6.20
0.120	20.15	6.80
0.200	21.18	7.02

TABLE IV

*Rate constant at 30°C for the  $H_2O_2$  decomposition at various solid catalyst concentrations*

Amount of catalyst used (g)	Rate constant ( $K \times 10^2 hr^{-1}$ ) for catalysts	
	$Al_2O_3-ZrO_2$ (500°C)	$Al_2O_3-TiO_2$ (420°C)
1.0	20.04	5.09
1.5	39.15	9.20
2.0	58.66	14.68
2.5	76.48	19.80

$H_2O_2$  has no effect on the rate of the reaction and K is constant. Similar experiments were tried with different quantities of the catalysts keeping the concentration of  $H_2O_2$  same. It is observed from Table IV that the values of K are directly proportional to the quantity of the catalyst used, suggesting that the decomposition of  $H_2O_2$  depends on the total acidity and basicity present on the surface of the catalyst.

Further work on the decomposition of  $H_2O_2$  with other mixed oxide catalysts on similar lines and a study of the mechanism of this reaction is in progress.

#### ACKNOWLEDGEMENTS

The authors wish to express their thanks to Bangalore University for the award of Research Scholarship to one of them (A. B. H.) and to Dr. M. Shadaksharaswamy, Prof. T. D. Bhaskar, and Prof. G. K. N. Reddy, for providing facilities and encouragement.

#### REFERENCES

- Chopra, B., Sandle, N. K., and Ramakrishna, V. (1970). The decomposition of  $H_2O_2$  in the presence of Bi-oxide-Mo-oxide catalysts. *Z. anorg. allg. Chem.*, **376**, 107.
- Deren, J., and Haber, J. (1965). The mechanism of low temperature doping of chromium oxide with altermvalent ions. *J. Catal.*, **4**, 22.
- Fisher, J. B., and Sebba, F. (1961). Relation between acidity of silic2-alumina and activation energy for the formic acid decomposition. *Actas int. Congr. Catalyse, Paris*, **1**, 711.
- Grossner, K., Hite, R., and Koerner, D. (1971). Reproducibility of the heterogeneously caalysed decomposition of  $H_2O_2$ . *Z. phys. Chem. Frankf.*, **74**, 67.
- Halgeri, A. B. (1972). Studies in acid and base properties and catalytic activity of some mixed oxide catalysts. *Ph.D. Thesis*, Bangalore University, Bangalore.
- Johnson, O. (1955). Acidity and polymerization activity of solid acid catalyst. *J. phys. Chem.*, **59**, 827.
- Krause, A. (1965). Beryllium-chrom (III)—*Mischhydroxide und deren Katalytisches Verhalten*. *Mh. Chem.*, **96**, 959.
- Matsuzaki, I., and Fukuda, Y. (1970). The effect of moisture adsorption on the acidity distribution of acid sites of silica-alumina. *J. Res. Inst. Catal. Hokkaido Univ.*, **17**, 192.
- Nikolesku, I. V., and Chiok, N. (1969). Investigation of the  $Al_2O_3$ - $ZrO_2$  catalysts system, Effect of heat treatment on infrared spectra and activity in the a-butene isomerization reaction. *Kinet. Katal.*, **10**, 910.
- Welvekar, S. P., and Halgeri, A. B. (1973). Decomposition of  $H_2O_2$  in presence of mixedoxide catalysts. *Z. anorg. allg. Chem.*, **400**, 83.