

The Decomposition of H_2O_2 in Presence of Mixed Oxide Catalysts

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With 2 Figures

Abstract. The decomposition of H_2O_2 in presence of $\text{TiO}_2\text{—ZrO}_2$ (ignited to various temperatures), $\text{SiO}_2\text{—ZrO}_2$, $\text{Al}_2\text{O}_3\text{—ThO}_2$, $\text{SiO}_2\text{—ThO}_2$, $\text{Al}_2\text{O}_3\text{—MoO}_3$, $\text{SiO}_2\text{—MoO}_3$, $\text{Al}_2\text{O}_3\text{—WO}_3$ and $\text{SiO}_2\text{—WO}_3$ mixed oxide catalysts 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. Both these sites catalyse the decomposition of H_2O_2 . The energy of activation values E_a and E_b are inversely proportional to the acidity and basicity values. The mechanism of decomposition of H_2O_2 in presence of acidic and basic sites is of similar nature. Only acid sites having an acid strength in the range of pK_a values $< +3.3$ and > -3.0 are able to catalyse the decomposition of H_2O_2 . Basic centres which are strong as well as those which are moderately weak ($\text{pK}_a \geq 10$) are able to catalyse.

Die Zersetzung von H_2O_2 in Gegenwart von Mischoxid-Katalysatoren

Inhaltsübersicht. Es wird die Zersetzung von H_2O_2 in Gegenwart verschiedener Mischoxid-Katalysatoren (s. o.) untersucht. Da diese bifunktionell sind, wurde durch Inhibitoren versucht, die Wirkung der sauren und basischen Zentren getrennt zu messen. K_a , aufgetragen gegen die Säurestärke, und K_b , aufgetragen gegen die Basenstärke, ergaben Geraden. Daraus wird geschlossen, daß beide Zentren die Zersetzung katalysieren. Die Werte der Aktivierungsenergien sind umgekehrt proportional den Säure- bzw. den Basenwerten. Der Zersetzungsmechanismus ist in beiden Fällen ähnlich. Zur Katalyse sind nur fähig Zentren mit Säurestärken von $\text{pK}_a < +3,3$ und > -3 . Die basische Katalyse erstreckt sich von Zentren sehr starker bis mäßig schwacher Basizität ($\text{pK}_a \geq 10$).

Introduction

The study of the properties of mixed oxide catalysts has been undertaken by a large number of workers. In view of the usefulness of the decomposition of H_2O_2 to obtain information regarding the bifunctional behaviour of oxide catalysts, it was considered of interest to study this reaction with these catalysts for which no data exists.

An attempt has been made to evaluate the amount of decomposition 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. The work on decomposition of H_2O_2 has been further extended to propose a mechanism based on the bifunctional behaviour of these catalysts and also to provide useful information regarding active acidic and basic centres present on the surface.

Experimental

Reagents. Merck's quality H_2O_2 which was purified by distillation at reduced pressure was used in this investigation. All other chemicals used in this investigation were pure quality chemicals.

Preparation of catalysts. The mixed oxide catalysts were prepared by precipitation and impregnation technique¹). The mixtures of the precipitated hydroxides and impregnated oxides were digested for several hours and then filtered, washed and dried at 120°C for 20 hours. The samples thus obtained were powdered and only such samples collected between 100 to 150 mesh sieves were preserved. The powders were subjected to heat treatment in the temperature range 120°C to 1000°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 glass tubes.

Measurement of surface acidity and basicity. The acidity of these mixed oxides were measured by amine titration method²) in benzene using p-dimethylaminoazobenzene ($pK_a = +3.3$) 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 solution³).

Kinetic studies. 100 ml of 0.2 M solution of H_2O_2 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, temperature variation being $\pm 0.01^\circ C$. 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 0.01 M $KMnO_4$ solution at regular intervals of time.

Experiments were carried out with 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 surfaces and that both these sites catalyse the decomposition of H_2O_2 , an attempt has been made to evaluate the amount of the decomposition brought about by the acidic as well as the basic centres. For this purpose the acidic sites were poisoned by neutral red 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 surface⁴). Neutral red and HCl were selected for the purpose of

¹) K. SHIBATA, T. KIYOURA and K. TANABE, *J. Res. Inst. Catalysis, Hokkaido Univ.*; **18**, 189 (1970).

²) O. JOHNSON, *J. phys. Chem.* **59**, 827 (1955).

³) A. B. HALGERI, Ph. D. Thesis, Bangalore University, India (1972).

⁴) S. P. WALVEKAR and A. B. HALGERI, Paper presented to the Convention of Chemists, Bombay, India, p. 131 (1971).

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 H₂O₂.

Since the decomposition of H₂O₂ is a very sensitive reaction⁵⁾, 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 K (the rate constant for the catalyst as a whole), K_a and K_b (rate constants for the acidic and basic sites), the energy of activation values E_a, E_b (for acidic and basic sites) were calculated from the initial slopes of the rate curves $\log(a - x) \rightarrow t$, which were straight lines. These values are presented in Tables 1 and 2.

Table 1 Decomposition of H₂O₂ in presence of TiO₂-ZrO₂ (68-32%) catalyst

Sl. No.	Temperature of ignition °C	Acidity m.moles/g at pKa = 3.3	Basicity m.moles/g	Rate constant, hr ⁻¹						E _a calories per mole	E _b calories per mole
				K · 10 ² at		K _a · 10 ² at		K _b · 10 ² at			
				30°C	40°C	30°C	40°C	30°C	40°C		
1	2	3	4	5	6	7	8	9	10	11	12
1	120	0.11	0.60	20.0	31.0	3.1	6.1	16.0	25.0	12860	8420
2	220	0.16	0.50	18.2	29.0	4.0	8.0	13.6	21.5	11760	8680
3	360	0.20	0.26	10.3	19.0	5.2	8.6	6.9	11.5	9570	9680
4	440	0.11	0.19	9.2	13.9	2.9	5.6	5.1	8.6	12430	9900
5	520	0.12	0.15	7.8	11.0	2.9	5.7	4.6	7.9	12400	10240
6	600	0.10	0.11	6.2	9.2	2.1	4.2	3.0	5.8	13140	12490
7	700	0.02	0.08	3.5	6.0					Reactions too slow	
8	800	0.02	0.03	3.5	5.0					Reactions too slow	
9	1000	nil	nil								

The plots of K_a against acidity and K_b against basicity (Fig. 1 and 2) are straight lines, which implies⁴⁾ that both acidic and basic sites bring about the decomposition of H₂O₂. The sum of K_a and K_b is nearly equal to K for all catalysts except for binary oxides containing molybdena and tungstic oxide, where K_a is nearly equal to K. This is because, these catalysts have no strong basic sites on their surface as is proved by the fact that they do not adsorb phenol and when poisoned with neutral red (pKa ≤ +6.8) are unable to decompose H₂O₂.

It is also observed that E_a and E_b are inversely proportional to the acidity and basicity respectively (Tables 1 and 2).

The above observations and our earlier work³⁾ suggest that (i) acidic as well as basic sites bring about the decomposition of H₂O₂ and (ii) the mechanism of decomposition of H₂O₂ in presence of acidic and basic sites is

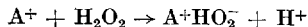
⁵⁾ K. GOSSNER, R. HITE and D. KORNER, Z. physik. Chem. [Frankfurt], **74**, 67 (1971).

Table 2 Decomposition of H_2O_2 in presence of various mixed oxide catalysts

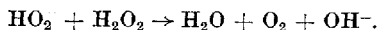
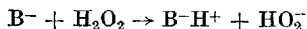
Sl. No.	Catalyst	Temperature of ignition °C	Acidity m.moles/g at pKa=3.3	Basicity m.moles/g	Rate constant, hr ⁻¹						E _a Calories per mole	E _b Calories per mole
					K · 10 ² at		K _a · 10 ² at		K _b · 10 ² at			
1	2	3	4	5	30°C	40°C	30°C	40°C	30°C	40°C	12	13
1	Silica-Zirconia (89-11%)	200	0.08	0.21	6.2	13.0	1.60	3.40	5.5	9.0	14110	8810
2	Silica-Zirconia (89-11%)	380	0.10	0.14	6.5	11.0	2.30	4.30	3.7	6.1	11750	9387
3	Silica-Zirconia (89-11%)	500	0.10	0.10	6.0	10.0	2.60	4.51	2.8	4.6	10286	9340
4	Alumina-Thoria (72-28%)	400	0.25	0.60	24.0	37.0	6.5	10.5	16.5	25.1	8995	7008
5	Silica-Thoria (85-15%)	400	0.10	0.30	11.5	17.1	3.0	4.3	8.0	12.2	6745	7907
6	Alumina-Molybdena (74-26%)	450	0.13	Nil	3.5	5.8	3.5	5.5	—	—	8511	—
7	Silica-Molybdena (81-19%)	450	0.14	Nil	4.1	6.0	4.0	6.0	—	—	7603	—
8	Alumina-Tungstic oxide (84-16%)	400	0.12	Nil	3.0	4.4	2.8	4.5	—	—	8892	—
9	Silica-Tungstic oxide (84-16%)	400	0.14	Nil	3.9	6.9	3.8	5.9	—	—	8690	—

of a similar nature. On the basis of the observations made above the following mechanism is proposed for the decomposition of H_2O_2 ,

i) for acidic sites:



ii) for basic sites:



In the above mechanism it is important to note that the mechanism is similar in both cases. The HO_2^- formed being responsible for the decomposition of H_2O_2 .

Experiments tried with TiO_2 which has acidity at $pK_a > +3.3$ and none at $pK_a = +3.3$, $Al_2O_3-SiO_2$ which has acid strength of $pK_a \leq -8.2$

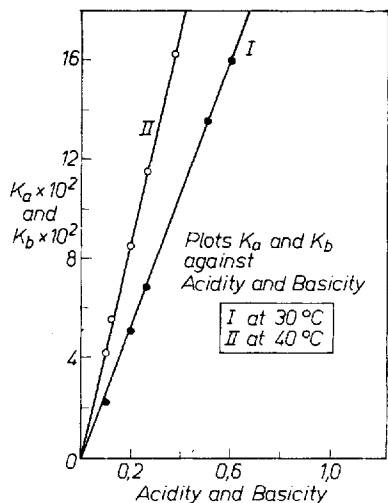


Fig. 1. The dependence of catalytic activity for decomposition of H_2O_2 on the number of acidic and basic centres of titania-zirconia catalyst

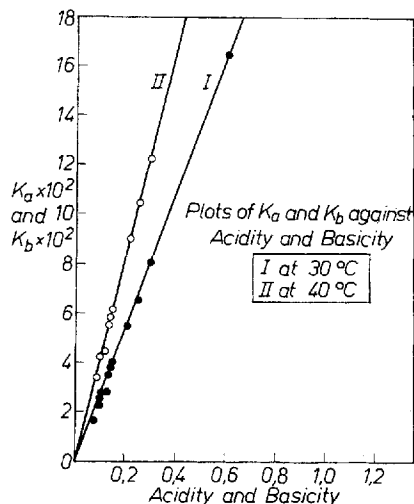


Fig. 2. The dependence of catalytic activity for decomposition of H_2O_2 on the number of acidic and basic centres of mixed-oxide catalysts (Table 2)

and H_3PO_4 supported on silica which has acid strength of $\text{pK}_a \leq -5.7^6$) show that these catalysts are unable to decompose H_2O_2 . It has been observed earlier that water poisons all acid sites of $\text{pK}_a \leq -3.0^7$) and hence in aqueous solutions sites with acid strength of $\text{pK}_a \leq -3.0$ are ineffective in the decomposition of H_2O_2 and sites with acid strength in the range with $\text{pK}_a \leq +3.3$ and $\text{pK}_a \geq -3.0$ are able to catalyse the decomposition of H_2O_2 .

Both phenol and H_2O_2 have a pK_a value in the range 9 to 11⁸). The basicity values of the surface of the catalysts measured by the phenol adsorption method should correlate well with the decomposition of H_2O_2 , and it has been found to be so. Basic sites of $\text{pK}_a \geq 10$ are able to decompose H_2O_2 . Weaker sites are unable to do so as H_2O_2 having a pK_a value in the range 9 to 11 needs stronger basic sites for it to react. This is proved by the fact that neutral red ($\text{pK}_a = +6.8$) is unable to decompose H_2O_2 .

Very strong acid sites on the surface of the catalyst either get poisoned by water⁷) or stabilise H_2O_2 by supplying H^+ ions as follows:



⁶) H. A. BENESI, *J. physic. Chem.* **61**, 970 (1957).

⁷) I. MATSUZAKI and Y. FUKUDA, *J. Res. Inst. Catalysis, Hokkaido Univ.* **17**, 192 (1970).

⁸) F. A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry. A Comprehensive Text", p. 373, Interscience Publishers, London 1967.

or the HO_2^- is very firmly held on the surface and is not available for the decomposition reaction. Acid sites of medium strength with $\text{pK}_a \leq +3.3$ do not suffer from the above two drawbacks, they react with H_2O_2 and HO_2^- is adsorbed on the surface. Since the acid site is of medium strength the HO_2^- adsorbed on the surface is available for reaction with H_2O_2 as depicted in the mechanism discussed earlier.

Thus it is evident that basic sites of strength with $\text{pK}_a > 10$ and acid sites in the range of $\text{pK}_a < +3.3$ and > -3 are catalytically active for the decomposition of H_2O_2 in aqueous solutions.

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