

Catalytic decomposition of hydrogen peroxide on fine particle ferrites and cobaltites

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MS received 10 April 1987; revised 23 June 1987

Abstract. The kinetics of heterogeneous decomposition of hydrogen peroxide on fine particle ferrites, MFe_2O_4 and cobaltites, MCo_2O_4 , where $M = Mn, Fe, Co, Ni, Zn$ and Mg , have been investigated. The decomposition of H_2O_2 was found to be first order at low concentration (0.3%) and zero order at high concentration (30%) of H_2O_2 . The catalytic activity of cobaltites on the decomposition of H_2O_2 is found to be better than ferrites. The observed catalytic behaviour of ferrites and cobaltites has been attributed to their fine particle nature, large surface area and electronic structure.

Keywords. Hydrogen peroxide decomposition kinetics; ferrites; cobaltites.

1. Introduction

The kinetics of decomposition of hydrogen peroxide has been studied by a large number of workers (Schumb *et al* 1955). The interest in the kinetics of H_2O_2 decomposition stems from its use in oxygen production, power generation and electrolytic reduction of oxygen in which H_2O_2 is an intermediate. The choice of a suitable catalyst for the decomposition of H_2O_2 has proved to be difficult due to the high cost of catalysts like silver oxide, platinum and palladium black as well as the poor reactivity of cheap catalysts like MnO_2 , Co_2O_3 , Fe_2O_3 etc. Recently, Onuchukwu (1984), Goldstein and Tseung (1974) and Cota *et al* (1964) have reported that ferrites; cobalt-iron oxide spinels ($Co_xFe_{3-x}O_4$, $x = 0-3$) in particular, show high activity in the decomposition of H_2O_2 . The catalytic activity of these oxides has been attributed to their electronic structure, composition, surface morphology and microstructure (surface area).

It is rather surprising that although Co-Fe oxide spinels have been investigated in great detail there is only one report (Tarasevich and Efremov 1980) on the use of cobaltites, MCo_2O_4 , where $M = Mn, Co, Ni$ and Mg , as catalysts for the decomposition of H_2O_2 . It has been observed that $NiCo_2O_4$ dispersed over carbon black exhibits maximum activity for H_2O_2 decomposition and catalytic activity is attributed to the increased dispersedness of cobaltites on carbon black. Therefore, it was considered interesting to study the heterogeneous decomposition of H_2O_2 in the presence of fine particle ferrites, MFe_2O_4 , and cobaltites, MCo_2O_4 , where

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M = Mn, Fe, Co, Ni, Zn and Mg. The choice of these catalysts is warranted by the fact that they have large surface areas (12–140 m²/g) and are prepared by the low temperature decomposition of novel hydrazine precursors N₂H₅M_{1/3}M'_{2/3}(N₂H₃COO)₃H₂O, M = Mn, Fe, Co, Ni, Zn and Mg; M' = Fe or Co. The novelty of the precursors is their autocatalytic combustion behaviour, with the evolution of large amounts of gases, leaving behind fine particle oxides (Ravindranathan and Patil 1987; Ravindranathan *et al* 1987).

2. Experimental

2.1 Preparation of the oxides

The preparation and characterisation of hydrazine precursors to fine particle ferrites, N₂H₅M_{1/3}Fe_{2/3}(N₂H₃COO)₃H₂O (Ravindranathan and Patil 1987) and cobaltites N₂H₅M_{1/3}Co_{2/3}(N₂H₃COO)₃H₂O (Ravindranathan *et al* 1987), where M = Mn, Fe, Co, Ni, Zn and Mg, have already been described. Only the preparation of fine particle ferrites and cobaltites is described here.

Ferrites: The precursors N₂H₅M_{1/3}Fe_{2/3}(N₂H₃COO)₃H₂O were ignited in a silica crucible and allowed to decompose autocatalytically in the absence of a flame or an external heat source. The crystals decompose with the evolution of NH₃, H₂O, N₂, H₂, and CO₂. The decomposition products, ferrites (MFe₂O₄), are fine, voluminous residues.

Cobaltites: The precursors N₂H₅M_{1/3}Co_{2/3}(N₂H₃COO)₃H₂O were ignited in a silica crucible and allowed to decompose autocatalytically as described above. The decomposition products, cobaltites (MCo₂O₄), were also fine in nature.

Some important properties like XRD data, particle size, BET surface area (determined by N₂ adsorption at liquid nitrogen temperature) of ferrites and cobaltites have been summarised in table 1.

Table 1. Some properties of fine particle ferrites and cobaltites.

Compound	XRD data				
	a* (nm)	Crystallite size (nm)	Particle density (g/cm ³)	Particle size (micron)	Surface area (m ² /g)
MgFe ₂ O ₄	0.8388	13	4.118	3.15	114
MnFe ₂ O ₄	0.8321	6	3.269	1.65	140
CoFe ₂ O ₄	0.8418	10	3.649	2.5	116
NiFe ₂ O ₄	0.8359	22	3.574	3.2	26
ZnFe ₂ O ₄	0.8477	9	3.437	3.4	108
MgCo ₂ O ₄	0.8130	10	3.0517	2.20	47
MnCo ₂ O ₄	0.8113	24	5.46	0.82	24
FeCo ₂ O ₄	0.8222	6.5	3.919	4.35	116
NiCo ₂ O ₄	0.8118	10	5.7	—	12.4
ZnCo ₂ O ₄	0.8172	14	5.06	4.56	65

* Powder diffraction file, Inorganic vol. PDIS-10iRB, Joint Committee on Diffraction standards, Pennsylvania: 1967.

2.2 Kinetics of H_2O_2 decomposition

Stabiliser free H_2O_2 (AnalaR BDH, 30% w/v) solution was used in all the experiments. The solution was standardised by standard $KMnO_4$ before the run. The kinetics of H_2O_2 decomposition was studied using 30% and 0.3% solutions. Precautions were taken to protect the solutions from light and heat during storage.

A schematic diagram of the experimental set-up used is shown in figure 1. This is a slightly modified version of the gasometric method (Deren *et al* 1963). The catalyst is taken in the reaction vessel which is immersed in a thermostat. To the side limb of the reaction vessel is attached a 'V' shaped tube, well-protected from light, containing the H_2O_2 solution. The reaction rate is deduced in terms of the volume of oxygen evolved in the liquid phase. The oxygen evolved is measured with the help of the manometer filled with water coloured with potassium dichromate. As oxygen is collected in the manometer, the water level in the right arm lowers while it rises in the left. In a given interval of time the difference in water levels in the arms of the manometer, which is proportional to the amount of O_2 evolved, can be determined by running down water from the burettes at the left. The large burette of 50 ml capacity is used to drain off larger volumes while the smaller 10 ml capacity is used to make minor corrections.

In a typical experiment, a few milligrams of the catalyst were placed in the reaction vessel and attached to the set-up. About 10 ml of the H_2O_2 solution were poured into the 'V' tube, which was attached to the reaction vessel. The reaction vessel and the 'V' tube were immersed in thermostat maintained at $30^\circ C \pm 0.5^\circ C$ and atmospheric pressure. The whole set-up was left undisturbed till the reaction vessel and the tube attained thermal equilibrium. During this time, O_2 evolved due to self-decomposition of H_2O_2 , was adjusted by bringing the manometric liquid to the initial level before the start of the run. After equilibrium the H_2O_2 solution was

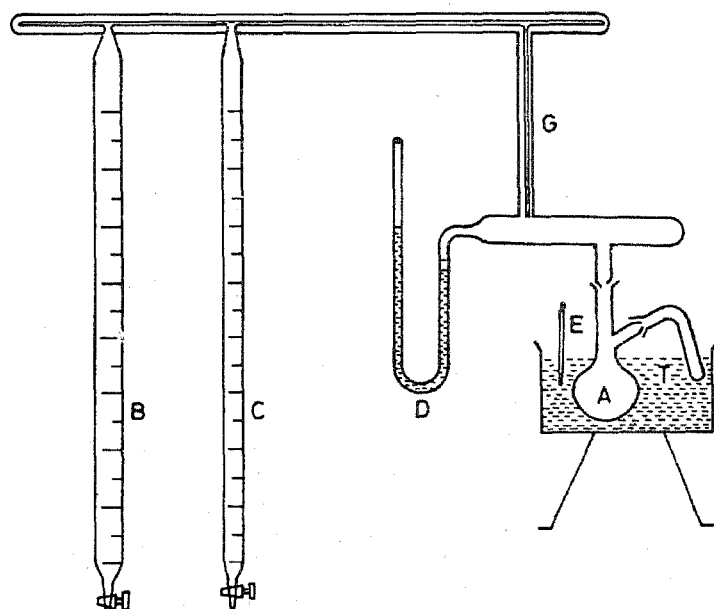


Figure 1. Experimental set-up for the determination of catalytic activity of H_2O_2 decomposition: A—reaction vessel; B—50 ml burette; C—10 ml burette; D—manometer; E—thermometer; T—thermostat; G—capillary tube.

poured into the reaction vessel by rotating the 'V' tube through 90°. A stop watch was simultaneously started to monitor the time. The entire mixture was stirred, using a magnetic stirrer, during the course of the reaction. At regular intervals of time, the burette readings were noted which indirectly measured the volume of O₂ evolved in terms of the rise of manometric liquid. In the case of ferrites, 10 mg of the sample were taken whereas in the case of cobaltites 5 mg of the sample were sufficient to study the reaction kinetics. (With 10 mg of cobaltites, the amount of O₂ evolved was so large and rapid that, in a fraction of a second the manometric liquid flew out; thus hindering proper measurements.)

3. Results and discussion

The characterization and particulate properties of ferrites and cobaltites are summarized in table 1. The XRD data clearly show that the oxides have a spinel structure and the observed a values correspond to those reported in the literature. The crystallite sizes calculated from X-ray line broadening using Debye-Scherrer formula (Klug and Alexander 1954) are in the range of 6–24 nm. The particle size and surface area values range from 0.8–4.6 μ and 12–140 m²/g, respectively, and clearly show that the particles are very fine and therefore can be expected to be highly reactive. In fact the reactivity of these fine particles was seen in the ability of ferrite powders to achieve almost theoretical density when sintered \sim 1000°C. However, the large surface area of these oxide materials can be expected to find application in heterogeneous catalytic reactions, and as a test, the kinetics of H₂O₂ decomposition has been investigated. As the oxides were ultrafine in nature, the kinetics of H₂O₂ decomposition could not be studied using the KMnO₄ titrimetric method (Keating *et al* 1965) because of the difficulty in the separation of the dispersed fine ferrite particles in H₂O₂.

The plots of volume of oxygen V (ml) evolved versus time t (min) for H₂O₂ (30%) decomposition in the presence of ferrite and cobaltite are shown in figures 2a & b, respectively. The specific rate constants K_s , mol⁻¹s⁻¹gm⁻¹ with \pm 5%

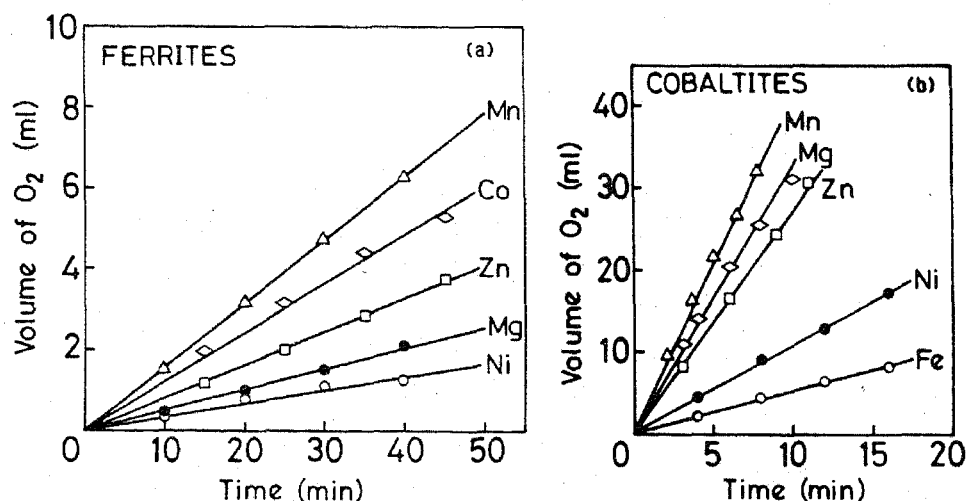


Figure 2. Decomposition of H₂O₂ (30%) on (a) ferrites, (b) cobaltites, at 30°C.

Table 2. Rate constants for H₂O₂ decomposition on ferrites and cobaltites.

Catalysts	Zero-order rate constants		First-order rate constants	
	$K_s(\text{mol l}^{-1} \text{s}^{-1} \text{ gm}^{-1})$ at 30°C		$K_s(\text{s}^{-1} \text{ gm}^{-1})$ at 30°C	
MnFe ₂ O ₄	0.259		0.2612	
CoFe ₂ O ₄	0.196		0.2316	
NiFe ₂ O ₄	0.053		-	
ZnFe ₂ O ₄	0.139		-	
MgFe ₂ O ₄	0.074		0.0676	
Fe ₃ O ₄	0.0268		-	
MnCo ₂ O ₄	6.57		0.33	
FeCo ₂ O ₄	0.854		-	
NiCo ₂ O ₄	1.784		-	
ZnCo ₂ O ₄	4.49		0.2288	
MgCo ₂ O ₄	5.36		0.632	
Co ₃ O ₄	1.25		-	

error, corrected for self-decomposition of H₂O₂ (30%) i.e. a blank run without the catalyst (O₂ evolution rate at 30°C $1.6 \times 10^{-4} \text{ ml s}^{-1}$) are given in table 2. A linear $V-t$ plot is indicative of reaction kinetics which are zero order with respect to H₂O₂.

In the second set the decomposition kinetics with 0.3% H₂O₂ was found to follow a rate law which was first order with respect to H₂O₂. The results are shown in figures 3a and 3b, expressed in the form of a $\log V_{\infty} - V_0 / V_{\infty} - V_t$ versus time (min) plot, where V_0 is the volume of oxygen evolved at time $t = 0$, V_{∞} is the maximum volume of oxygen evolved at time (t) gave linear plots. The specific rate constants $K_s \text{ s}^{-1} \text{ gm}^{-1}$ ($\pm 5\%$ error, corrected for self-decomposition of H₂O₂) are given in table 2. The reaction rate was monitored in the initial kinetic region,

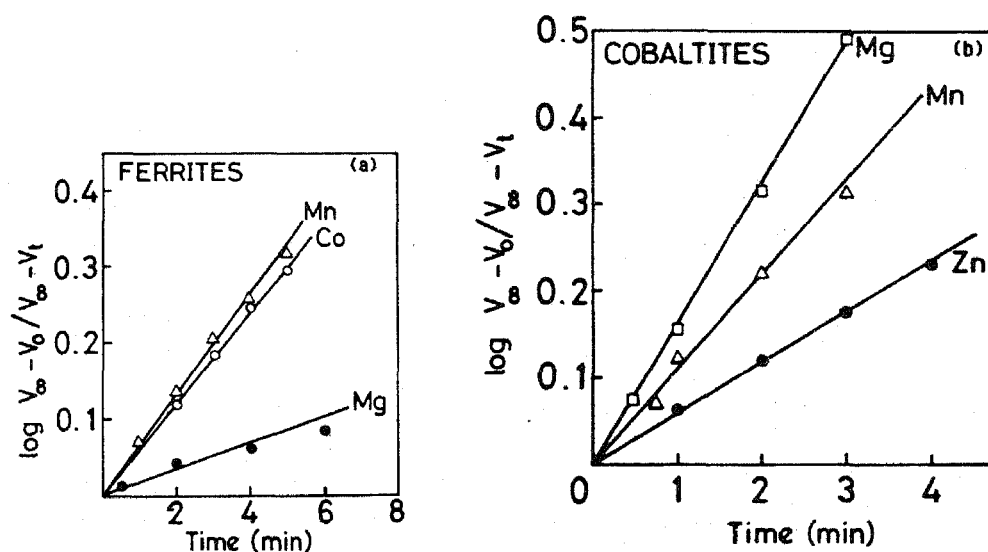
Figure 3. Decomposition of H₂O₂ (0.3%) on (a) ferrites, (b) cobaltites, at 30°C.

Table 3. Activation energies for ferrites and cobaltites.

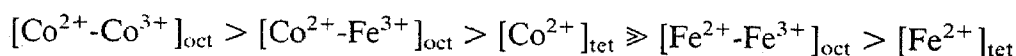
Catalyst	Rate constant K_s s ⁻¹ g ⁻¹			E_a kcal/mol
	$K(308^\circ\text{K})$	$K(313^\circ\text{K})$	$K(318^\circ\text{K})$	
<i>Ferrites</i>				
MgFe ₂ O ₄	0.056	0.099	0.120	9.15
MnFe ₂ O ₄	0.384	0.673	0.741	12.32
CoFe ₂ O ₄	0.305	0.360	0.47	8.39
<i>Cobaltites</i>				
MgCo ₂ O ₄	1.87	3.12	-	16.6
MnCo ₂ O ₄	1.08	1.3	-	11.04
FeCo ₂ O ₄	0.078	0.086	0.096	4.19
NiCo ₂ O ₄	0.066	0.115	0.187	19.78
ZnCo ₂ O ₄	0.370	0.545	-	17.03

whereafter the first-order plots lose its linearity. This may be due to the formation of gas pockets in the solid catalyst which may mask the activity of potential sites as encountered earlier (Cota *et al* 1964). The reaction rate constants were found to be independent of the initial H₂O₂ concentration (0.3%) characterising the first-order kinetics.

The energy of activation for the first-order kinetics were also calculated, the values of which range from 7–19 kcal mol⁻¹ as shown in table 3.

The consequences of the reaction kinetics studied at two different concentrations: 30% and 0.3% has led to the conclusion that manganese and magnesium ferrites and cobaltites are quite promising as catalysts. The inactivity of large surface area oxides, ZnFe₂O₄ and FeCo₂O₄, at lower concentrations of H₂O₂ (0.3%) appears to indicate that an optimum concentration of H₂O₂ is essential. This could in turn mean that the initial concentration of peroxide is also a matter of importance in governing the catalytic behaviour of the oxides.

The observed catalytic activity appears to be proportional to the surface area of the oxides. Thus a large surface area and a fine particle nature of the catalysts favour the heterogeneous decomposition of H₂O₂. However, when comparing the order of reactivity in a given set of ferrites or cobaltites with the order of surface areas, some discrepancies are observed which can be explained in terms of the electronic structure and surface morphology of the spinels, that is, the distribution of M²⁺ and Fe³⁺ or Co³⁺ ions in the tetrahedral or octahedral sites in the spinel. Another important feature observed is that the cobaltites, having lower surface areas, are much more active than the ferrites. This may be explained in terms of the better electron-hopping ability of Co²⁺ or Co³⁺ species in the octahedral sites of spinels. The high reactivity of the MnFe₂O₄ and MnCo₂O₄ could also be speculated upon in similar terms. The redox couple [Mn²⁺-Fe³⁺] and [Mn²⁺-Co³⁺] appear to have even greater potentiality than



reported earlier (Goldstein and Tseung 1974).

Since most catalytic decompositions of H₂O₂ have been studied in the presence of KOH, which is known to control the reaction kinetics, a representative

experiment was done with CoFe_2O_4 using KOH. The observed rate constant ($K = 0.4545 \text{ s}^{-1} \text{ g}^{-1}$) is much higher than the value reported earlier ($K = 0.120 \text{ s}^{-1} \text{ g}^{-1}$) (Goldstein and Tseung 1974). This suggests that the fine particle ferrites and cobaltites prepared by the low temperature precursor technique have better catalytic activity than conventional oxides.

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