

KINETICS OF HYDROGEN PEROXIDE DECOMPOSITION ON A Fe_2O_3 - MoO_3

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Kinetics of H_2O_2 decomposition on a Fe_2O_3 - MoO_3 (wt. ratio 2 : 3.8) catalyst was investigated at two concentrations of H_2O_2 (1.2 and 2.4 wt. %) and in the temperature range 25–45°C. Also the effect of catalyst concentration was studied. An induction period was observed which duration depended on the temperature used.

The catalytic decomposition of hydrogen peroxide to water and oxygen in the presence of simple metal oxides¹⁻⁴ as well as mixed oxide catalysts⁵⁻⁹ has been studied extensively. It was established that the catalytic activity of simple oxides can be altered by addition of other metal oxides⁵. Further on, it was shown¹⁰⁻¹² that the activities of oxide catalysts depend on the method of their preparation.

Kawaguchi et al.⁴ studied the effect of surface excess oxygen of some metallic oxides (TiO , ZnO , V_2O_5 , Co_3O_4 , NiO , PbO and MoO_2) on the catalytic activity for H_2O_2 decomposition. The activity at 30–50°C increased with increasing surface excess oxygen. Similar results were also observed in the case of Cr_2O_3 and Cr_2O_3 - Al_2O_3 catalysts¹³⁻¹⁶. Similarly, the physicochemical properties of the binary catalyst NiO - CeO_2 were found¹² to be affected by the method of preparation of the metal oxide catalyst. The NiO - CeO_2 samples from cerium(III) nitrate and from cerium(IV) ammonium nitrate were compared and found to be affected considerably by the nature of precursor. Nevertheless, in spite of the differences, the catalytic decomposition of H_2O_2 on the catalysts from both series seems to proceed on catalytic centre of the same kind¹².

In most cases the H_2O_2 decomposition on mixed oxide obeys first order rate equation. Sometimes, a departure of the first order kinetics was observed only in the initial stage of the reaction^{17,18} in the sense of retardation. In further stages of the decomposition, the first order patterns were obeyed. The first order kinetics was not observed in H_2O_2 decomposition using NiO - MoO_3 (ref.¹⁷), NiO - V_2O_5 (ref.¹⁸) and reduced cobalt oxide catalysts¹⁹. Rao et al.²⁰ studied the kinetics of

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H_2O_2 decomposition on NiO , Fe_2O_3 and $\text{NiO-Fe}_2\text{O}_3$ two-component catalysts and in all cases a first order rate equation was found to fit the experimental data. Similarly, Múčka et al.²¹ showed that the decomposition of H_2O_2 over NiO-ZnO two-component catalyst is first order reaction with respect to H_2O_2 concentration.

Kohler et al.²² investigated the $\text{MnO}_2\text{-Al}_2\text{O}_3$ catalyst for the catalytic decomposition of H_2O_2 in a continuous tubular packed bed reactor and the first order kinetics was indicated by the conversion-time curves. In the present paper we have studied the activity of the $\text{Fe}_2\text{O}_3\text{-MoO}_3$ (2 : 3.8) catalyst for H_2O_2 decomposition as a test reaction.

EXPERIMENTAL

All the chemicals used were either of BDH (Analaor) or E. Merck (GR) grade.

The catalyst $\text{Fe}_2\text{O}_3\text{-MoO}_3$ (2 : 3.8)^{23,24} was prepared by coprecipitation from $\text{Fe}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ solution with an ammonium molybdate solution $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ at constant pH 1.5 and temperature 60°C. The obtained precipitate was washed with distilled water till became free from NH_4^+ ions, dried at 115°C and calcined at 500°C for 5 h.

H_2O_2 solutions were prepared²⁵ by mixing 3.5 ml, 7.0 ml and 10.5 ml of 30% H_2O_2 , respectively, with bidistilled water to obtain a total volume of dilute H_2O_2 of 100 ml in concentrations 1.2, 2.4 and 3.6%. The concentration of H_2O_2 was determined by titration against standard KMnO_4 solution.

The catalytic activity of the prepared catalyst for H_2O_2 decomposition²⁵ was evaluated in the liquid phase. The catalyst samples were added to a stirred thermostated vessel containing 100 ml of H_2O_2 of known concentration. The temperature of H_2O_2 solution was kept constant at the desired level within $\pm 0.2^\circ\text{C}$ by means of an ultrathermostat and a double jacketed cell. Weighed catalyst was added to the H_2O_2 solution at constant stirring conditions. The initial concentration of H_2O_2 as well as its concentration at regular intervals were determined by transferring 0.5 ml samples to a flask containing 10 ml of 1M- H_2SO_4 acid solution and titrated against standard solution of KMnO_4 until a pink end point was reached.

RESULTS AND DISCUSSION

The catalytic decomposition of H_2O_2 over the $\text{Fe}_2\text{O}_3\text{-MoO}_3$ catalyst (2 : 3.8) was carried out at constant initial concentration of H_2O_2 (1.2% and 2.4%) in the presence of variable amounts of catalyst (0.3, 0.7, and 1.0 g) and at 25 and 35°C. The same study was carried out at 45°C using the same initial concentrations of H_2O_2 and with three different weights of catalyst (0.1, 0.3, and 0.5 g). The obtained time curves are shown in Fig. 1. In the initial period, the reaction is very slow. However in all experiments the decomposition of H_2O_2 increased with time and depended on the amount of catalyst. The reaction rate increased with the temperature.

We assume that the induction period is due to the formation of active centres as a result of the interaction of Mo^{6+} with Fe^{2+} to give the active Mo^{5+} ions. The induction period was found to be affected by both the amount of catalyst and the temperature, decreasing with the amount of the catalyst and temperature.

The first order plots $\log(a - x)$ vs t are shown in Fig. 2 (a is initial concentration of H_2O_2 , x its concentration at time t). An autocatalytic process can be clearly distinguished from Figs 1 and 2, but at higher conversions the reaction follows the first order kinetic equation. Therefore the autocatalytic first order relationship could be applied. In coordinates of Fig. 3, straight lines were obtained in all cases. From the slopes and intercepts of these straight lines the values of the rate constant of the autocatalytic first order equation^{19,26} k_0 (reaction rate constant on the fresh catalyst) and k_1 (reaction rate constant involving a side reaction step²³) were evaluated. The found values of k_0 and k_1 are summarized in Table I. The values of both con-

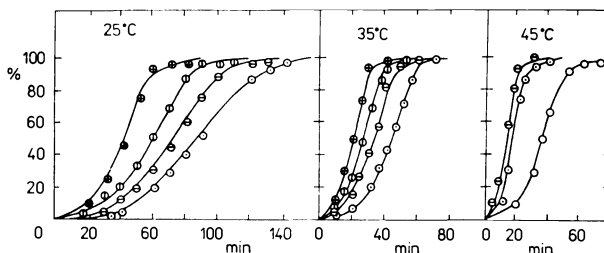


FIG. 1

Decomposition-time curves of H_2O_2 over $\text{Fe}_2\text{O}_3\text{-MoO}_3$ catalyst at constant initial concentration of H_2O_2 (1.2%), at different temperatures and with various weights of catalyst (in g): \circ 0.1, \odot 0.3, \ominus 0.5, \oplus 0.7, \oplus 1.0

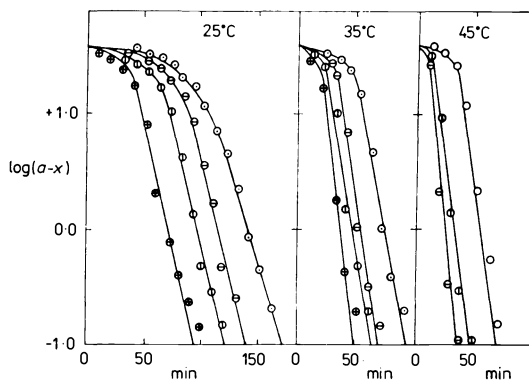


FIG. 2

First order plots of the decomposition of H_2O_2 over $\text{Fe}_2\text{O}_3\text{-MoO}_3$ catalyst at constant initial concentration of H_2O_2 (1.2%), at different temperatures and with various weights of catalyst (in g): \circ 0.1, \odot 0.3, \ominus 0.5, \oplus 0.7, \oplus 1.0

stants k_0 and k_1 increase with increasing amount of catalyst as well as with increasing temperature. Arrhenius plots were obtained for k_0 and k_1 in the temperature range 25–45°C and with variable amounts of catalyst (Fig. 4). The activation energies E_0 and E_1 were evaluated from the slopes of the straight lines, and their values are given in Table I. E_1 is smaller than E_0 indicating that the decomposition of H_2O_2 occurs more readily on the partially reduced surface (i.e. on the surface containing Mo^{5+} ions).

The thermodynamic parameters ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger were determined as follows: the change in the free energy of activation ΔG^\ddagger was evaluated from the Eyring's

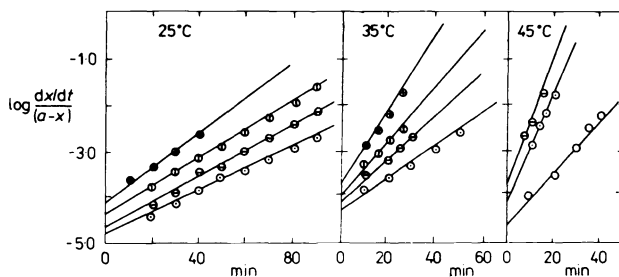


FIG. 3

Autocatalytic first order plots of H_2O_2 decomposition over Fe_2O_3 - MoO_3 catalyst at constant initial concentration of H_2O_2 (1.2%), at different temperatures and with various weights of catalyst (in g): \circ 0.1, \square 0.3, \triangle 0.5, \diamond 0.7, \oplus 1.0

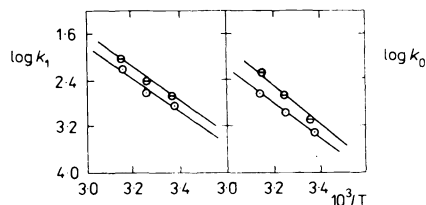


FIG. 4

Arrhenius plots for the decomposition of H_2O_2 (1.2%) over Fe_2O_3 - MoO_3 catalyst with various weights of catalyst (in g): \circ 0.3, \square 0.5

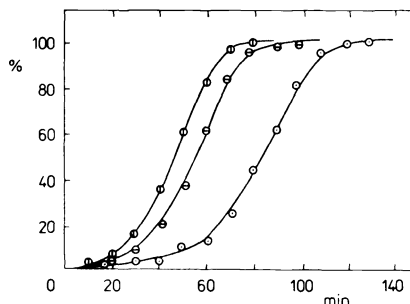


FIG. 5

Decomposition-time curves of H_2O_2 over Fe_2O_3 - MoO_3 catalyst at constant initial concentration of H_2O_2 (2.4%), at 25°C with various weights of catalyst (in g): \circ 0.3, \square 0.5, \triangle 0.7

TABLE I

Activity of $\text{Fe}_2\text{O}_3\text{-MoO}_3$ (2 : 3·8) catalyst in the decomposition of H_2O_2 at different experimental conditions and at initial concentration of H_2O_2 1·2%

Run No.	Weight of cat., g	Temp. °C	$k_0 \cdot 10^3 \text{ min}^{-1}$	$k_1 \cdot 10^3 \text{ min}^{-1}$	$E_0 \text{ kJ mol}^{-1}$	$E_1 \text{ kJ mol}^{-1}$	$\Delta G_0^\ddagger \text{ kJ mol}^{-1}$	$\Delta G_1^\ddagger \text{ kJ mol}^{-1}$	$\Delta H_0^\ddagger \text{ kJ mol}^{-1}$	$\Delta H_1^\ddagger \text{ kJ mol}^{-1}$	$\Delta S_0^\ddagger \text{ J mol}^{-1}$	$\Delta S_1^\ddagger \text{ J mol}^{-1}$	$t_{\text{ind}} \text{ min}$
1	0·3	25	0·55	1·57	59·9	52·5	93·5	90·3	57·3	49·9	-117	-131	100
2	0·3	35	1·09	2·45									50
3	0·3	45	2·18	7·08									19
4	0·5	25	0·77	1·98	61·8	53·2	91·7	89·7	59·2	50·7	2 613	-127	75
5	0·5	35	2·17	3·27									33
6	0·5	45	5·88	9·81									13
7	0·7	25	1·94	2·17	61·5	56·0	90·5	90·3	59·0	53·2	2 614	-119	58
8	0·7	35	4·34	4·52									27
9	1·0	25	2·44	2·80	66·1	58·6	89·8	88·7	63·6	56·1	-85	-106	43
10	1·0	35	5·80	6·03									21
11	0·1	45	0·87	3·80									42

TABLE II

Activity of $\text{Fe}_2\text{O}_3\text{-MoO}_3$ (2 : 3·8) catalyst in the decomposition of H_2O_2 at different experimental conditions and at initial concentration of H_2O_2 2·4%

Run No.	Weight of cat., g	Temp. °C	$k_0 \cdot 10^3 \text{ min}^{-1}$	$k_1 \cdot 10^3 \text{ min}^{-1}$	$E_0 \text{ kJ mol}^{-1}$	$E_1 \text{ kJ mol}^{-1}$	$\Delta G_0^\ddagger \text{ kJ mol}^{-1}$	$\Delta G_1^\ddagger \text{ kJ mol}^{-1}$	$\Delta H_0^\ddagger \text{ kJ mol}^{-1}$	$\Delta H_1^\ddagger \text{ kJ mol}^{-1}$	$\Delta S_0^\ddagger \text{ J mol}^{-1}$	$\Delta S_1^\ddagger \text{ J mol}^{-1}$	$t_{\text{ind}} \text{ min}$
1	0·3	25	0·35	0·83	52·3	45·7	95·0	93·0	50·2	43·2	-146	-128	90
2	0·3	35	0·69	1·51									50
3	0·5	25	0·69	1·23									60
4	0·7	25	1·09	1·65									50

equation²⁷ $k = kT/h \exp(-\Delta G^\ddagger/RT)$, where k and h are the Boltzmann and the Planck constants, respectively. The change in the enthalpy of activation ΔH^\ddagger was calculated from the relationship²⁷: $\Delta H^\ddagger = E - RT$. The change of entropy of activation ΔS^\ddagger was estimated according to the relation: $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, where T is the mean value of the absolute temperature within the temperature range (298–318 K). The calculated values are given in Table I.

The second series of this study was carried out at constant initial concentration of H_2O_2 equal to 2.4% (w/w) and two different temperatures 25 and 35°C and by using variable amount of catalysts (0.3, 0.5, and 0.7 g). The results obtained show the same behaviour described previously. The values of thermodynamic parameters are summarized in Table II.

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