J.RADIOANAL.NUCL.CHEM.,LETTERS 103 /5/ 281-290 /1986/

INFLUENCE OF ^{60}Co GAMMA RADIATION ON La_2CuO_4 CATALYST FOR THE DECOMPOSITION OF HYDROGEN PEROXIDE

S. Balasubrahmanyam, B. Viswanathan, V.R.S. Rao, J.C. Kuriacose

Department of Chemistry,
Indian Institute of Technology,
Madras - 600 036, India

Received 11 November 1985
Accepted 25 November 1985

The catalytic activity of La_2CuO_4 for the decomposition of H_2O_2 was studied in detail. La_2CuO_4 was prepared by the ceramic method in four different ways. Gamma irradiation of the La_2CuO_4 samples increased their catalytic activity irrespective of the method of preparation. The enhanced catalytic activity is attributed to irradiation generated Cu^+ centres on the surface of the catalyst.

INTRODUCTION

In the present investigation the previously reported work on the influence of γ-radiation on La_2CuO_4 /Ref. 1/ has been extended to a study of the kinetics and catalysis of La_2CuO_4 in the decomposition of H_2O_2.

EXPERIMENTAL

The preparation of La_2CuO_4 and its characterization have been described in an earlier paper[1]. The samples were irradiated in Petri dishes in air in a 5000 Ci ^{60}Co

Elsevier Sequoia S. A., Lausanne
Akadémiai Kiadó, Budapest

γ-cell, having a dose rate of 0.4 Mrad/h supplied by BARC, Bombay.

The kinetics of decomposition of H_2O_2 was followed titrimetrically:

The H_2O_2 solution was standardized with $KMnO_4$ before each experiment. The decomposition reaction was carried out in glass stoppered conical flasks /50 ml capacity/. 20 ml of H_2O_2 solution of required concentration /0.18-0.16M/ was taken in the conical flask. After keeping the flask in the thermostat adjusted to the required temperature /70±0.1 °C/, a known weight of the catalyst /0.2 g/ was added. At different time intervals 1 ml of solution was withdrawn taking care not to disturb the catalyst layer.

RESULTS AND DISCUSSION

The catalytic activities of four different La_2CuO_4 samples as measured by the initial rates of decomposition of H_2O_2 are given in Table 1. It is seen from Table 1 that the four La_2CuO_4 samples have almost the same catalytic activity indicating that the method of preparation has no significant influence on the reaction.

The reaction was carried out at various initial concentrations of H_2O_2 ranging from 0.18M to 0.50M with a constant weight of the catalyst /0.2 g/, keeping the temperature constant at 70±0.1 °C. The order of the reaction with respect to H_2O_2 was determined from the slope of the plot of logarithm of initial rates vs. logarithm of initial concentrations of H_2O_2 /Fig. 1./. The reaction was of first order with a rate constant, $k = 4.2 \times 10^{-3}$ min^{-1}.

The amount of La_2CuO_4 was varied in the range 0.15-0.4 g keeping all other parameters constant, and the initial

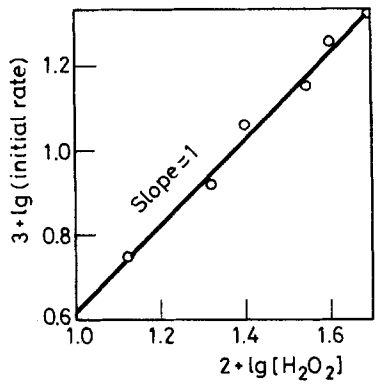

Fig. 1. Effect of $[H_2O_2]$ on the reaction. Weight of La_2CuO_4 = 0.2 g; Vol. of H_2O_2 solution = 20 ml; Temperature = 70±0.1 °C; Sample - OA

TABLE 1

Catalytic activities of La_2CuO_4 samples prepared by different methods

$[H_2O_2]$ = 0.18M; Weight of La_2CuO_4 = 0.2 g; Volume of H_2O_2 solution = 20 ml; Temperature = 70±0.1 °C

Sample No.	Samples	Catalytic activity mol l^{-1} min^{-1}
1.	La_2O_3 - CuO /OA/	3.7×10^{-3}
2.	LaOxal-CuOxal /OB/	3.2×10^{-3}
3.	LaOxal-CuO /OC/	4.1×10^{-3}
4.	La_2O_3 - CuOxal /OD/	4.0×10^{-3}

rates were determined in each case. The initial rate values were plotted against the weight of the catalyst used in the reaction /Fig. 2./. It can be seen that the rate of the reaction increases with an increase in the amount of the catalyst.

The influence of γ-irradiation on the catalytic activity of the four La_2CuO_4 samples was studied by the above

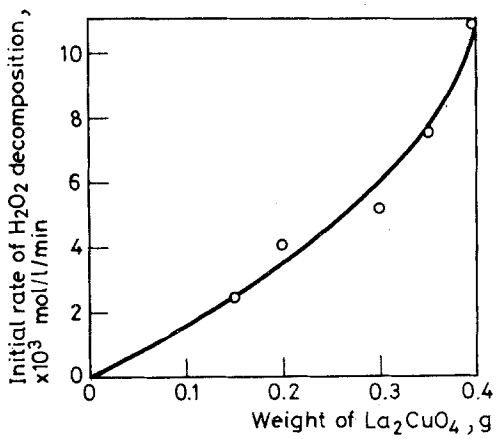

Fig. 2. Effect of the amount of catalyst on the reaction. $[H_2O_2]$ = 0.24M; Temperature = 70±0.1 °C; Sample - OB

procedure using the irradiated catalyst. It is seen from the results presented in Table 2 that there is an enhancement in the catalytic activity of the four samples with an increase in γ-dose.

Generally the irradiation of the catalyst was carried out by exposing the solid sample to γ-radiation in presence of air which contains nitrogen, oxygen, traces of moisture and CO_2. These gases may have significant influence on the changes brought about in the catalyst during irradiation. To investigate the effect of components of air, the irradiation of the catalyst was carried out in vacuum and in the presence of nitrogen, dry oxygen, moist oxygen, dry carbon dioxide, moist carbon dioxide, and moisture free from CO_2. Sample OA was chosen for the above experiments.

From the results presented in Table 3, it is seen that when the catalyst was irradiated in vacuum, nitrogen, dry oxygen and dry CO_2, there was no significant change in the catalytic activity. When the catalyst was, however, irradiated in oxygen or CO_2 containing traces of moisture or

TABLE 2

Effect of ^{60}Co γ-radiation on the catalytic activity of La_2CuO_4 in the decomposition of H_2O_2. $[H_2O_2]$= 0.18M; Weight la La_2CuO_4 = 0.2 g; Volume of H_2O_2 solution = 20 ml; Temperature = 70±0.1 °C; γ-dose rate = 0.4 Mrad h^{-1}

Time of γ-irradiation, days	γ-dose, Mrads	Initial rates of decomposition, mol l^{-1} min^{-1} Sample OA	Sample OB	Sample OC	Sample OD
-	-	3.7×10^{-3}	3.2×10^{-3}	4.1×10^{-3}	4.0×10^{-3}
7	67.2	5.7×10^{-3}	6.1×10^{-3}	7.1×10^{-3}	6.0×10^{-3}
14	134.4	8.4×10^{-3}	1.1×10^{-2}	1.2×10^{-2}	1.0×10^{-2}
21	201.6	1.4×10^{-2}	2.2×10^{-2}	2.0×10^{-2}	2.0×10^{-2}
30	288.0	2.9×10^{-2}	2.8×10^{-2}	4.0×10^{-2}	4.2×10^{-2}
35	336.0	2.9×10^{-2}	3.0×10^{-2}	4.0×10^{-2}	4.2×10^{-2}

TABLE 3

Effect of γ-irradiation of La_2CuO_4/OA/ on its catalytic activity in various gas atmospheres

$[H_2O_2]$ = 0.16M; Weight of catalyst = 0.2 g; Volume of H_2O_2 solution = 20 ml; Temperature = 70±0.1 °C; γ-dose rate = 0.4 Mrad h^{-1}; Total γ-dose = 192 Mrads

No.	Treatment	Catalytic activity /initial rate/, mol l^{-1} min^{-1}
1.	Unirradiated	3.5×10^{-3}
2.	γ-irradiated in vacuum	3.5×10^{-3}
3.	γ-irradiated in nitrogen	3.5×10^{-3}
4.	γ-irradiated in dry oxygen	3.5×10^{-3}
5.	γ-irradiated in moist oxygen	6.6×10^{-3}
6.	γ-irradiated in dry CO_2	3.5×10^{-3}
7.	γ-irradiated in moist CO_2	8.0×10^{-3}
8.	γ-irradiated in moisture free from CO_2	6.6×10^{-3}

in presence of moisture free from CO_2 there was a significant increase in the catalytic activity. This indicates that moisture is necessary during irradiation for an enhancement in the catalytic activity. The energy of activation for sample OA was found to be 14.7 kcal/mol and 13.4 kcal/mol for unirradiated and γ-irradiated samples, respectively.

The effect of moisture and/or any other atmosphere on the catalytic activity was investigated as follows: Pellets of sample OA were irradiated in the γ-source with a dose rate of 0.4 Mrad h^{-1} in vacuum, dry nitrogen, dry oxygen, dry CO_2 and in presence of traces of moisture free from CO_2. The electrical conductivities were measured. The

TABLE 4

Measurement of electrical conductivity and catalytic activity of samples irradiated in various atmospheres

$[H_2O_2]$ = 0.16M; Weight of La_2CuO_4 = 0.2 g; Volume of H_2O_2 solution = 20 ml; Temperature = 70±0.1 °C

Sample	Electrical conductivity, σ, $ohm^{-1}\ cm^{-1}$	Catalytic activity, $mol\ l^{-1}\ min^{-1}$
Unirradiated	1.3×10^{-4}	3.5×10^{-3}
Irradiated in vacuum, dry nitrogen, dry oxygen and dry CO_2	1.3×10^{-4}	3.5×10^{-3}
Irradiated in moisture free from CO_2	2.0×10^{-3}	1.9×10^{-2}

catalytic activity of the irradiated samples for the decomposition of H_2O_2 was also determined.

The results given in Table 4 indicate that there is no change in the electrical conductivity of the samples irradiated in vacuum, dry nitrogen, dry oxygen, and dry CO_2. However, the sample irradiated in presence of moisture free from CO_2 indicated a significant enhancement in the electrical conductivity as well as in catalytic activity compared to that of unirradiated sample. This indicates that moisture plays a significant role during irradiation in the enhancement of electrical conductivity also.

For the catalytic decomposition of H_2O_2 on CuO Mučka[2] suggested that Cu^+ ions present in the oxide seem to play an important role as donor centers for the reaction. It is suggested that during irradiation more Cu^+ may be formed in the catalyst due to radiation damage. Since Cu^+ is an electron donor, the increase of its concentration in the

TABLE 5

Determination of Cu^+ content in catalyst irradiated in various atmospheres

$[H_2O_2]$ = 0.16M; Weight of La_2CuO_4 = 0.2 g; Volume of H_2O_2 solution = 20 ml; Temperature = 70±0.1 °C

Sample	Cu^+ content, %	Catalytic activity, mol l^{-1} min^{-1}
Unirradiated	0.3	3.5×10^{-3}
Irradiated in vacuum, dry nitrogen, dry oxygen and dry carbondioxide	0.3	3.5×10^{-3}
Irradiated in moisture free from CO_2	1.1	1.9×10^{-2}

solid due to irradiation is responsible for the enhancement of electrical conductivity. A significant increase in Cu^+ concentration was found[1] in the four La_2CuO_4 samples after an irradiation period of 30 days in air at a dose rate of 0.4 Mrad h^{-1} /Ref. 1/. Since irradiation results in an increase of Cu^+ concentration, electrical conductivity and catalytic activity, it can be concluded that there is a direct relation ship between the concentration of Cu^+ and the catalytic activity of the solid.

Sample OA was irradiated in vacuum, dry oxygen, dry nitrogen, dry CO_2 and in presence of traces of moisture free from CO_2 for 30 days at a dose rate of 0.4 Mrad h^{-1} and then the Cu^+ content and catalytic activity of these samples was determined.

The results shown in Table 5 indicate that, when the sample was irradiated in moisture free from CO_2 there was a significant increase in the Cu^+ content and catalytic

activity. This implies that it is only the moisture which is responsible for the increased formation of Cu^+ in the catalyst during irradiation. The increase of the number of Cu^+ centers is responsible for the enhancement in electrical conductivity and in catalytic activity.

REFERENCES

1. S. Balasubrahmanyam, B. Viswanathan, V.R.S. Rao, J.C. Kuriacose, J. Radioanal. Nucl. Chem., Letters 96 /1985/ 301.

2. V. Mučka, Coll. Czech. Chem. Commun., 41 /1976/ 1717.