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Catalytic decomposition of nitrous oxide on $Cu_xCo_{3-x}O_4$ spinels

R. Sundararajan and V. Srinivasan*
Department of Chemistry, Indian Institute of Technology, Madras 600 036 (India)

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Abstract

The catalyst series $Cu_xCo_{3-x}O_4$ $(0 \leqslant x \leqslant 1)$ was synthesised by the decomposition of nitrate precursors. Higher copper containing spinels $(x \geqslant 0.5)$ were in partially inverted forms. The decomposition of nitrous oxide was carried out at the initial pressures of 50 and 200 Torr (1 Torr = 133.3 Pa). Two regions of activity were observed based on the mechanism $x < 0.5$ and $x \geqslant 0.5$. The activity pattern has been explained on the basis of the number of active sites and solid state interactions. In both regions, the catalyst with the highest copper content was found to be less active.

Keywords: copper-cobalt oxide, nitrous oxide decomposition, catalyst preparation (thermal decomposition), kinetics.

INTRODUCTION

In recent years, studies of various ternary and quaternary oxides with spinel, perovskite and pyrochlore structures have increased their applicability to serve as suitable substitutes for noble metal catalysts in a variety of areas such as in pollution control, in electrocatalytic cell electrodes and in oxidation reactions [1-6].

Spinel oxides are a class of complex oxides with the composition AB_2O_4 where A ions are generally bivalent metal ions occupying the tetrahedral sites and the B ions are trivalent ions occupying the octahedral sites. Recently Angelov et al. [7] examined the activity of copper–cobalt spinels for the oxidation of carbon monoxide and concluded that the resistance of the catalyst towards sulphur dioxide poisoning increased due to the inverse distribution of ions. Mahandjiev et al. [8] have discussed the effect of the distribution of cations in $Cu_xCo_{3-x}O_4$ on the oxidation of carbon monoxide by nitric oxide. The study of the decomposition of nitrous oxide is considered as one of the best test reactions to evaluate the activity of oxide catalysts. A recent review by Larsson [9] summarises the results of nitrous oxide decomposition on oxide catalysts. This decomposition study gives us an idea about the effects of solid state and electronic properties of the catalysts on the oxidation reaction. In the present communication, the results of the decomposition of nitrous oxide on $Cu_xCo_{3-x}O_4$ spinels are presented.

EXPERIMENTAL

Preparation and characterisation of catalysts

The catalysts $Cu_xCo_{3-x}O_4$ ($x=0.0$, 0.2, 0.5, 0.8 or 1.0) were synthesized by the thermal decomposition of a mixture of metal nitrate precursors [7]. The aqueous solutions of $Cu(NO_3)_2 \cdot 6H_2O$ (AnalaR, Glaxo, India) and $Co(NO_3)_2 \cdot 6H_2O$ (AnalaR, BDH, India) were mixed in the stoichiometric proportions corresponding to different values of x in the final oxides. The mixture was evaporated to dryness on a water bath and the dried mass was heated at 573 K until the evolution of the nitrogen oxides ceased. This was followed by heating the sample at 623 K for six hours in an atmosphere of oxygen. The single phase formation of the catalysts was confirmed by X-ray diffraction (XRD).

The catalysts were characterised by XRD and electrical conductivity measurements. The surface areas of the catalyst were obtained by the BET method employing nitrogen adsorption at liquid nitrogen temperature.

Kinetic runs

The decomposition of nitrous oxide was tested in a glass static reactor fitted with a recirculatory system. About 1.5 g of the catalyst was used for the kinetic studies. The catalyst was subjected to the following pretreatments between kinetic runs: (i) Evacuation at 10^{-6} Torr (1 Torr = 133.3 Pa) at 623 K for six hours. (ii) Treatment with 100 Torr of oxygen at the reaction temperature. (iii) Mild evacuation at 10^{-3} Torr to remove the gas phase and weakly adsorbed oxygen.

The reactions were carried out at an initial pressure of 50 and 200 Torr of nitrous oxide, respectively, in the temperature range 423–533 K. The kinetics of the reaction were followed by monitoring the increase in pressure as a function of time.

Mechanism and kinetic equation

The mechanism of nitrous oxide decomposition on oxide catalysts has been investigated by Cimino and coworkers [10,11] who have put forward the following two kinetic equations:

$$-dPN_2O/dt = k\,PN_2O \qquad (1)$$

$$-dPN_2O/dt = k\, PN_2O/P_{O_2} \tag{2}$$

Eqn. (1) refers to no inhibition by product oxygen and eqn. (2) strong inhibition by product oxygen. The integral form of the above equations are, respectively, as follows:

$$\ln\frac{a}{a-x} = kt \tag{3}$$

$$(a/2)^{\frac{1}{2}}\ln\left(\frac{a^{\frac{1}{2}}+x^{\frac{1}{2}}}{a^{\frac{1}{2}}-x^{\frac{1}{2}}}\right) - (2x)^{\frac{1}{2}} = kt \tag{4}$$

Eqs. (3) and (4) have been utilised in the evaluation of rate constants.

RESULTS AND DISCUSSION

Solid state aspects

The lattice parameter (cation distribution in terms of inversion parameter) resistivity at room temperature and the surface area of the catalysts are presented in Table 1.

As far as copper cobaltites are concerned, controversies regarding their structure exist [12]. It was first thought that a cubic spinel could not be prepared with higher copper content. Rasines [13] synthesised $CuCo_2O_4$ in the normal cubic form, whereas Angelov et al. [7] synthesised it in the inverse cubic form. The XRD characterisation [14] studies in the present investigation show that the higher copper containing spinels ($x \geqslant 0.5$) are in the partially inverted forms.

Seebeck coefficient measurements indicated that all the catalysts possessed p-type charge carriers. Substitution of copper in Co_3O_4 led to a decrease in resistance (Table 1) up to $x = 0.5$, and the catalysts behaved like p-type semi-

TABLE 1

Structural and solid state parameters for the series $Cu_xCo_{3-x}O_4$

Catalyst	Lattice parameter (Å)	Inversion parameter$^{\alpha}$	Resistance at room temp. (Ω)	Surface area (m^2/g)
Co_3O_4	8.08	0.0	10000	7.32
$Co_{0.2}Co_{2.8}O_4$	8.09	0.0	2000	8.20
$Cu_{0.5}Co_{2.5}O_4$	8.11	0.25	1300	7.80
$Cu_{0.8}Co_{2.2}O_4$	8.12	0.4	1100	8.60
$CuCo_2O_4$	8.14	0.5	940	10.70

$^{\alpha}$Fraction of bivalent ion occupied in the O_h site, e.g.: $CuCo_2O_4$: $Cu^{2+}_{0.5}\,Co^{3+}_{0.5}\,(Cu^{2+}_{0.5}\,Co^{3+}_{1.5})O_4$.

conductors whereas above $x=0.5$, p-type semi-metallic behaviour has been observed as reported elsewhere [15].

In situ electrical conductivity studies during adsorption of nitrous oxide and oxygen showed a increase in the conductivity of the catalyst indicating that N_2O^- or O_2^- species are formed on the surface respectively.

Kinetic aspects

The decomposition of nitrous oxide on catalysts with $x<0.5$ obeyed eqn. (2) corresponding to the desorption of oxygen as the rate-controlling step, whereas those with $x \geqslant 0.5$ obeyed eqn. (1) with adsorption of nitrous oxide as the rate-limiting step. This observation is the same irrespective of the initial pressure of nitrous oxide on all catalysts in the present investigation. The typical kinetic

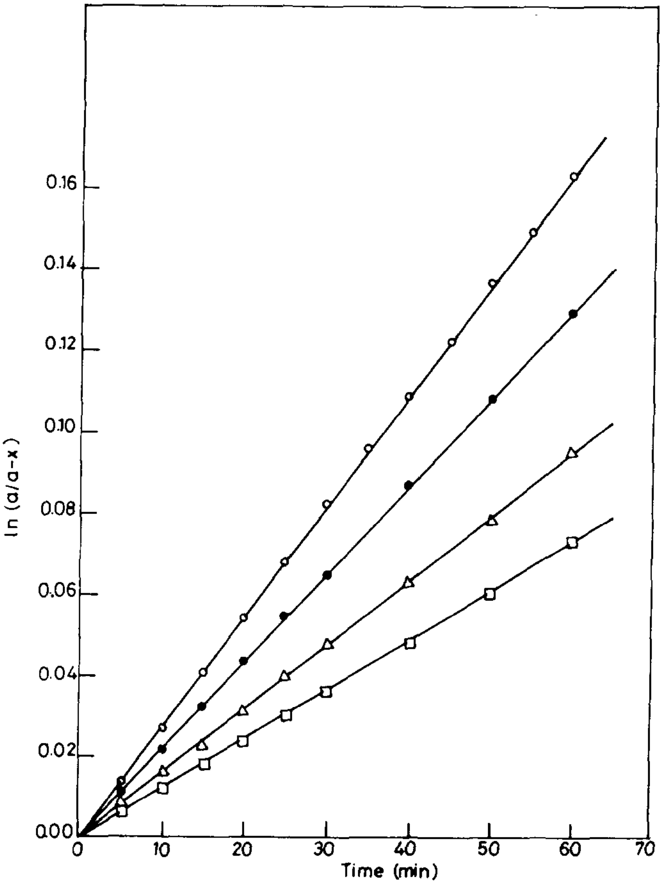

Fig. 1. Kinetic plots for the decomposition of nitrous oxide on $Cu_{0.5}Co_{2.5}O_4$ (○) 473 K, (●) 458 K, (△) 438 K, (□) 423 K.

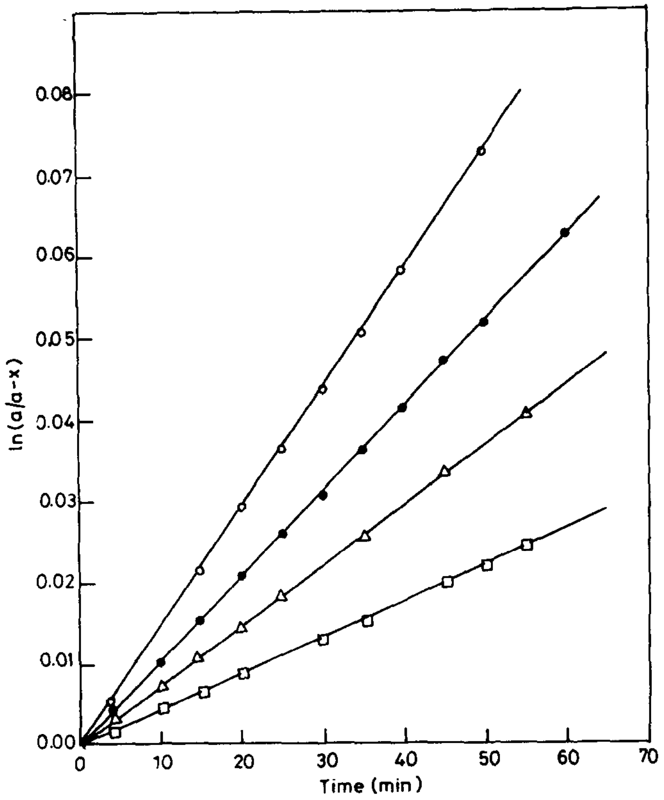

Fig. 2. Kinetic plots for the decomposition of nitrous oxide on $Cu_{0.5}Co_{2.5}O_4$ at 200 Torr. (○) 478 K, (●) 458 K, (○) 438 K, (□) 413 K.

plots for the decomposition of nitrous oxide at 50 and 200 Torr on $Cu_{0.5}Co_{2.5}O_4$ are shown in Figs. 1 and 2, respectively. The mechanism followed, energy of activation, ln *A* parameter, rate constant at 473 K and the percentage conversion at a chosen temperature, are presented in Table 2.

The discussion of the kinetic results of this paper is based on the following facts:

(1) Electron donating capacity of Cu^{2+} and Co^{2+}: Considering the electronic configuration of Cu^{2+} and Co^{2+}, it is obvious that adsorption is expected to be favoured on Co^{2+} as opposed to on Cu^{2+}.

(2) Effect of solid state interactions: In spinels, several interactions involving A and B ions are known. The interactions which are effective, considering the size of A and B ions and the angle, are A–O–B, B–O–B and B–B, whereas A–O–A interaction is negligible [16].

For the sake of discussing the results, the series could be divided into two regions based on the mechanism followed.

TABLE 2

Kinetic parameters for the series $Cu_xCo_{3-x}O_4$

Catalyst	Pressure (Torr)	No. of mechanism[α]	E_a (kJ/mol)	ln A	No. $k_{473} \times 10^3$	Conversion (%)[β]
Co_3O_4	50	II	13.5	0.004	11.71	30.0
	200		23.4	1.11	7.77	
$Cu_{0.2}Co_{2.8}O_4$	50	II	58.4	8.64	2.03	17.7
	200		38.9	3.55	1.73	
$Cu_{0.5}Co_{2.5}O_4$	50	I	27.0	0.92	2.60	11.5
	200		31.1	1.25	1.29	
$Cu_{0.8}Co_{2.2}O_4$	50	I	36.7	3.38	2.59	10.5
	200		54.5	7.05	1.04	
$CuCo_2O_4$	50	I	54.0	7.44	1.83	9.3
	200		56.8	7.49	0.97	

[α] No. of mechanism: I: No. inhibition by product oxygen. Unit of rate constant min^{-1}. II: Strong inhibition by product oxygen. Unit of rate constant $(mm)^{\frac{1}{2}} min^{-1}$.

[β] Conversion (%) at 523 K at 60 min and 200 Torr.

Region I

Region I is made up of the catalysts with composition $x=0.0$ and 0.2. Here the decomposition obeys kinetic eqn. (2) with desorption of oxygen as the rate-limiting path. This observation is supported by kinetic runs in the presence and in the absence of oxygen which showed a reduction in the rate constant in the former case, while maintaining the total initial pressure of the reaction constant. The fact that desorption of oxygen is rate-limiting in this region can be understood by considering Co^{2+} as the adsorption site, which has relative ease in donating an electron to the adsorbing molecule. In this region the catalyst which contains the highest cobalt content ($x=0.0$) was found to be the most active catalyst. This could be due to the presence of the high number of sites with a d^6–d^7 configuration. The higher activity of such a configuration, with one e^- transfer between the homo atoms, is not unexpected [17]. There is no change in the B site occupancy and hence its effect can not be observed in this region due to B–B or B–O–B interactions.

Region II

The catalysts with composition $x=0.5$, 0.8 and 1.0 form this region which followed eqn. (1), corresponding to the adsorption of nitrous oxide as rate-limiting. This could be due to the substitution of Co^{2+} by Cu^{2+} which does not facilitate electron transfer, relatively, for adsorption.

In this region the most active catalyst is the one with composition $x=0.5$. This could be due to the availability of the larger number of Cu^{2+} sites (responsible for nitrous oxide adsorption) on account of the decreased A–O–B and B–B interactions involving Cu^{2+}. A further increase in copper content would increase the A–O–B and B–B interactions involving copper at the A and B sites, resulting in the reduction in the number of adsorption sites. Hence the activation energy for the reaction increases with copper content.

Moreover partial occupation of Cu^{2+} in the Oh sites would push Co^{3+} to the tetrahedral sites. This would lead to a reduction in the Co^{2+}_{Td}-O-Co^{3+}_{oh} interaction which might also contribute to the reduction in the activity of the catalyst.

Before concluding this paper a comparison with the results of Mahandjiev et al. [8] on the interaction of carbon monoxide with nitric oxide on this series of catalysts is essential. According to them, an enhancement in the activity is observed upon inversion ($x \geqslant 0.5$). The difference in the observation may be due to the association mechanism for which the adsorption of carbon monoxide and nitric oxide on adjacent sites is essential, whereas, for the decomposition of nitrous oxides adsorption of nitrous oxide on adjacent sites is not feasible as oxygen has to be desorbed from the lattice.

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