JOURNAL OF MATERIALS SCIENCE 27 (1992) 1353–1356

Catalytic activity and XPS investigation of dalofossite oxides, $CuMO_2$ (M=Al, Cr or Fe)

J. CHRISTOPHER, C. S. SWAMY
Department of Chemistry, Indian Institute of Technology, Madras 600036, India

Catalytic decomposition of N_2O has been carried out on oxides having dalofossite structure $CuMO_2$; (M = Al, Cr or Fe) at 50 and 200 torr initial pressure of N_2O in the temperature range 380–480 °C. $CuFeO_2$ showed higher activity while $CuCrO_2$ showed low conversion in the temperature range studied. The variation in activity has been explained based on the presence of mixed valence copper and the concentration of copper on the surface as evinced from X-ray photoelectron spectroscopy.

1. Introduction

Mixed metal oxides are more advantageous compared to simple oxides because the crystal structure can accommodate various active transition metal ions and can stabilize unusual valence states of transition metal ions. Attempts have been made to evaluate the catalytic activity of mixed metal oxides having perovskite and spinel structure for various reactions [1–3]. Oxides having dalofossite structure are known to exhibit interesting structural and solid state properties [4–8]. In the present investigation, an attempt has been made to evaluate the catalytic activity of dalofossite oxides; $CuMO_2$ (M = Al, Cr or Fe), using decomposition of N_2O as the test reaction.

2. Experimental procedure

Oxides with the formula $CuMO_2$ were prepared by heating a stoichiometric mixture of CuO and M_2O_3 at 1050 °C for 48 h in a platinum crucible. The formation of single phase was confirmed by X-ray diffraction (XRD). The surface area of these oxides was determined by the BET method using nitrogen gas as the adsorbate at liquid nitrogen temperature. Magnetic susceptibility measurements were performed in a vibrating sample magnetometer (PAR 155) at room temperature employing a field strength of 5 kG.

The surfaces of these oxides were characterized by X-ray photoelectron spectroscopy (XPS). XPS were recorded using an ESCALAB Mark II at room temperature and a base pressure of 10^{-8} mbar. The carbon contamination peak at 285.0 eV was taken as internal standard.

Decomposition of N_2O was carried out on these oxides at 50 and 200 torr (1 torr = 1.333×10^2 Pa) initial pressures of N_2O in the temperature range 380–480 °C. Decomposition of N_2O on $CuCrO_2$ showed conversions less than 5% at 480 °C h^{-1} and hence kinetics could not be followed. However, the other two catalysts were found to be active and hence detailed kinetics were made.

3. Results and discussion

All the oxides are found to have dalofossite structure and the lattice parameters are given in Table I. The surface area of these oxides is very low which may be due to the sintering of particles due to the high temperature employed during synthesis.

The kinetic results were analysed using the rate Equations 1 and 2 corresponding to no inhibition and strong inhibition by oxygen, respectively [9]

$$\frac{-dP_{N_2O}}{dt} = k_1 P_{N_2O} \qquad (1)$$

$$\frac{-dP_{N_2O}}{dt} = \frac{k_2 P_{N_2O}}{P_{O_2}^{1/2}} \qquad (2)$$

Using the integrated forms of these equations, kinetic plots were made and a typical plot is shown in Fig. 1. Using the rate constants at different temperatures, Arrhenius plots were made (Fig. 2) and kinetic and Arrhenius parameters are summarized in Table II.

Based on the percentage conversion, the activity trend follows the order $CuFeO_2 > CuAlO_2 > CuCrO_2$. In order to explain the activity trend, the surfaces of the catalysts were analysed by XPS to obtain some idea about the active site and surface concentration of the active metal ions.

TABLE I Physico-chemical properties of $CuMO_2$

Property	$CuAlO_2$	$CuCrO_2$	$CuFeO_2$
Structure	Hexagonal	Hexagonal	Hexagonal
Lattice parameter (nm) a	0.287 51	0.297 09	0.302 24
c	1.694 10	1.710 05	1.704 95
Magnetic suceptibility, χ (e.m.u. g^{-1})	~ 10^{-7}	~ 10^{-6}	~ 10^{-4}
Surface area ($m^2 g^{-1}$)	1.1	1.4	1.0

0022-2461 © *1992 Chapman & Hall*

TABLE II Kinetic and Arrhenius parameters for the decomposition of N_2O

Catalyst	P_{N_2O}	T (°C)	k^a ($\times 10^3$)	E_a (k cal mol^{-1})	LnA	Decomposition at 440 °C, 30 min (%)
$CuAlO_2$	50	420	1.5	25.0	11.9	9.6
		440	3.3			
		460	4.7			
	200	400	1.1	27.2	13.2	5.8
		420	2.2			
		440	3.3			
		460	4.7			
$CuFeO_2$	50	400	1.2	16.9	5.9	10.8
		420	2.0			
		440	2.6			
		460	3.6			
	200	380	1.5	15.0	4.9	6.2
		400	2.1			
		420	2.6			
		440	3.9			
$CuCrO_2$	50 200	400–480 °C	–	–	–	< 5

[a] At 50 torr, unit of k is s^{-1} (Equation 1). At 200 torr, unit of k is $mm^{1/2} s^{-1}$ (Equation 2).

XPS of Cu 2p, Fe 2p, Al 2s and O 1s were recorded and the salient features of these spectra are summarized in Table III. Fig. 3 shows the Cu $2p_{3/2}$ spectrum of the oxides $CuMO_2$. The (Cu $2p_{3/2}$) XPS of $CuAlO_2$ has already been discussed elsewhere [10]. In the case of $CuAlO_2$ and $CuFeO_2$, Cu $2p_{3/2}$ spectra showed two peaks with binding energy values of ~ 932.8 and ~ 933.3 eV corresponding to Cu^+ and Cu^{2+}, respectively, as reported for several oxides containing copper [11,12]. The observation of a satellite

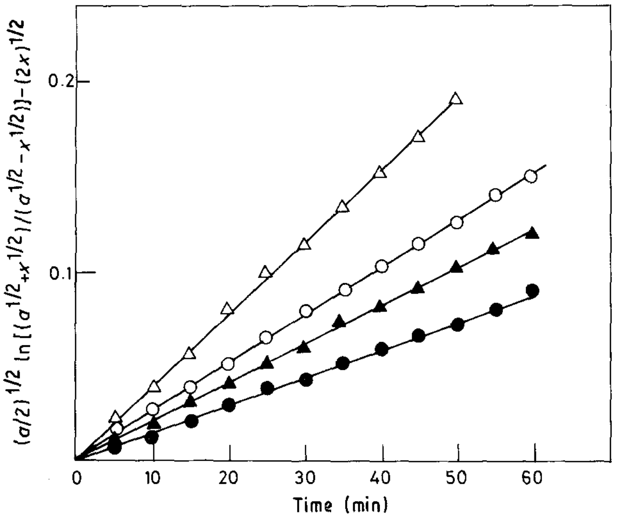

Figure 1 Kinetic plots for the decomposition of N_2O on $CuFeO_2$ at 200 torr. (△) 440 °C, (○) 420 °C. (▲) 400 °C (●) 380 °C.

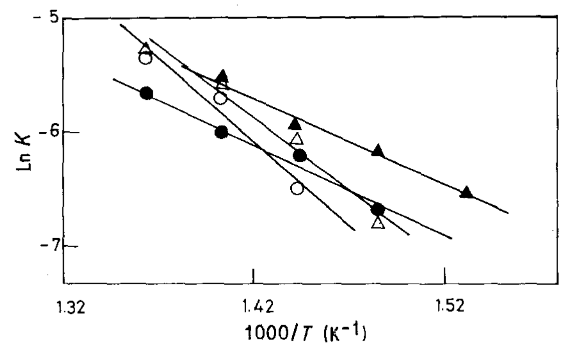

Figure 2 Arrhenius plots for the decomposition of N_2O. (●) $CuFeO_2$ (50 torr), (▲) $CuFeO_2$ (200 torr), (○) $CuAlO_2$ (50 torr), (△) $CuAlO_2$ (200 torr).

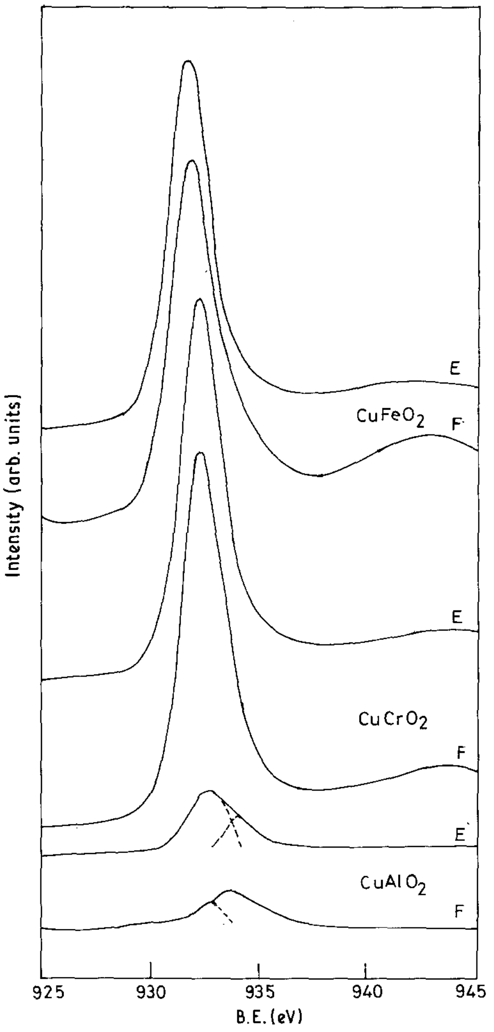

Figure 3 (Cu $2p_{3/2}$) XPS of $CuMO_2$. F, Fresh; E, etched.

TABLE III XPS data for the series $CuMO_2$

Region	Binding energy (eV)					
	$CuAlO_2$		$CuCrO_2$		$CuFeO_2$	
	Fresh	Etched	Fresh	Etched	Fresh	Etched
O 1s	529.50	–	530.25	530.50	529.90	530.35
	532.50	532.60	532.00	531.75	531.50	532.50
Cu $2p_{3/2}$	932.30	932.30	932.50	932.50	932.25	932.75
	933.10	933.40	–	–	933.75	–
Cu $2p_{1/2}$	broad	952.20	952.50	952.75	952.00	952.50
		952.70	–	–	954.00	–
Al 2s	118.40	118.30	–	–	–	–
Cr $2p_{3/2}$	–	–	576.50	576.50	–	–
Cr $2p_{1/2}$	–	–	586.25	586.25	–	–
Fe $2p_{3/2}$	–	–	–	–	711.50	711.40
$2p_{1/2}$	–	–	–	–	724.25	724.00
Surface Cu/M ratio	0.24	–	1.72	–	1.85	–

peak at ~ 942 eV is a clear indication of Cu^{2+} present on the surface. The presence of Cu^{2+} on the surface could be attributed to the partial oxidation of Cu^{+} on exposure to the atmosphere. However, after etching the surface with Ar^{+} for 1 min, the intensity of the Cu^{2+} peak at ~ 933.3 eV decreases or disappears. This is also evinced from the disappearance of the satellite peak observed for Cu^{2+}. This indicates that only few layers of the surface contain Cu^{2+}. On the other hand, the (Cu $2p_{3/2}$) XPS of $CuCrO_2$ showed a symmetrical peak with a binding energy value of ~ 932.5 eV corresponding to Cu^{+} on the surface.

Fig. 4 shows the O 1s core level spectra of these oxides. The XPS of all these oxides showed two peaks with binding energy values of ~ 530 and ~ 531.5 eV. According to the literature data for O 1s reported for several mixed metal oxides [13,14], the lower binding energy peak at ~ 530 eV corresponds to species with two negative charges O^{2-} while the higher energy peak is associated with oxygen species having one negative charge which includes CO_3^{2-}, or OH^-, O^-. However, the symmetrical C 1s peak observed for these oxides rules out the possibility of carbonate type species on the surface. It is evident from the binding energy values given in Table III that aluminium, chromium and iron are found to be present in trivalent state [11, 15–17].

Generally at low pressure, N_2O adsorption occurs preferentially by the interaction of π^* orbitals of N_2O with the surface states of the oxide lattice and because of limited surface sites, the adsorption of N_2O becomes rate controlling. This is also evidenced from the observation that at 50 torr, adsorption of N_2O is rate limiting (Equation 1). At high N_2O pressures a multicentre adsorption leads to the population σ^* orbital of N_2O and hence causes easy N–O fission resulting in a situation where desorption of oxygen controls the overall rate, which is the case at 200 torr N_2O (Equation 2). The catalytic activity of $CuAlO_2$ for the decomposition of N_2O has been discussed elsewhere [10]. Although the p-type nature of the dalofossite oxide [8] favours the adsorption of N_2O, its subsequent desorption of oxygen demands empty d-orbitals on the surface. The closed shell configuration of Al^{3+} and Cu^{+} is not favourable for the desorption of oxygen. Thus, Al^{3+} and Cu^{+} cannot act as sites for oxygen desorption. However, the observed activity could be attributed to the presence of Cu^{2+} as evinced from XPS studies. Also, desorption of oxygen which

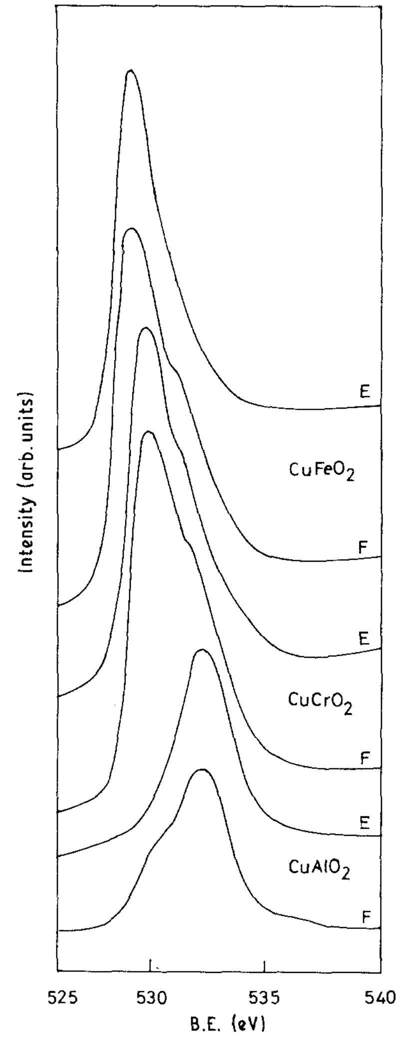

Figure 4 (O 1s) XPS of $CuMO_2$. F, Fresh; E, etched.

involves decoupling of spins will be easy on oxides having high moment. $CuAlO_2$, which showed weak paramagnetism due to the presence of small amounts of Cu^{2+}, does not favour this process. Similarly, XPS results of $CuFeO_2$ showed the presence of Cu^+ and Cu^{2+} and iron in the trivalent state. It is known that iron in the trivalent state is active for various reactions including the decomposition of N_2O [1]. Thus, the high activity of $CuFeO_2$ could be attributed to the presence of two active sites, namely Cu^{2+} and Fe^{3+}. Also, the desorption of oxygen will be easy on $CuFeO_2$ because of its high magnetic moment. Hence low E_a was observed. The (Cu 2P) XPS of $CuCrO_2$ showed the presence of only Cu^+ and Cr^{3+}. Because there is no Cu^{2+} on the surface and oxides containing Cr^{3+} are reported to be poor catalysts [18,19], $CuCrO_2$ showed poor conversion in the temperature range studied.

It is evident from Table III that $CuFeO_2$ has a higher concentration of copper on the surface and hence high activity. Although $CuCrO_2$ has a higher concentration of copper compared to $CuAlO_2$, it is less active compared to $CuAlO_2$ due to the absence of Cu^{2+} on the surface.

4. Conclusion

The catalytic activity of oxides having dalofossite structure has been tested using the decomposition of N_2O. The high activity of $CuFeO_2$ has been explained based on the presence of mixed valence nature and surface concentration of copper.

Acknowledgements

One of the authors (J.C.) thanks the CSIR, New Delhi, for a research fellowship. The authors thank RSIC, IIT, Madras, for recording the XPS.

References

1. L. G. TEJUCA, J. L. G. FIERRO and J. M. D. TASCON, *Adv. Catal.* **26** (1989) 237.
2. S. ANGELOV, E. ZHECHEVA and G. TYNELIEV, *React. Solids* **3** (1987) 57.
3. P. A. SERMAN and R. R. RAJARAM, *J. Chem. Soc. Farad. Trans. 1* **84** (1988) 391.
4. R. D. SHANNON, D. B. ROGERS and C. T. PREWITT, *Inorg. Chem.* **10** (1971) 713.
5. *Idem., ibid.* **10** (1971) 719.
6. *Idem., ibid.* **10** (1971) 723.
7. J. DOUMERC, A. WICHAINCHI, A. AMMAR, M. POUCHARD and P. HAGENMULLER, *Mater. Res. Bull.* **21** (1986) 745.
8. F. A. BENKO and F. P. KOFFYBERG, *J. Phys. Chem. Solids* **48** (1987) 431.
9. A. CIMINO, V. INDOVINA, F. PEPE and F. S. STONE, *Gazz. Chim. Ital.* **103** (1972) 935.
10. J. CHRISTOPHER and C. S. SWAMY, *J. Mol. Catal.* **62** (1990) 69.
11. C. D. WAGNER, in "Practical Surface Analysis by Auger and Photoelectron Spectroscopy", edited by D. Briggs and M. P. Seah (Wiley, New York, 1983).
12. A. LOSEV, K. KOSTOV and G. TYULIEV, *Surf. Sci.* **213** (1989) 564.
13. M. S. HEGDE, T. S. SAMPATH KUMAR and R. M. MALLYA, *ibid.* **188** (1987) 255.
14. P. SALVADOR, J. L. FIERRO, J. AMADOR, C. CASCALES and I. RASSINES, *J. Solid State Chem.* **81** (1989) 240.
15. P. SELVAM, B. VISWANATHAN, C. S. SWAMY and V. SRINIVASAN, *Ind. J. Technol.* **25** (1987) 639.
16. M. E. LEVIN, M. SALMERON, A. T. BELL and G. A. SOMORJAI, *Surf. Sci.* **195** (1988) 429.
17. G. C. ALLEM, M. T. CURTIS, A. J. HOOPER and P. M. TUCKER, *J. Chem. Soc. Dalton Trans.* (1973) 1675.
18. J. L. G. FIERRO and L. G. JEJUCA, *J. Catal.* **87** (1984) 126.
19. G. KREMENIC, J. M. L. NIETO, J. M. D. TASCON and L. G. TEJUCA, *J. Chem. Soc. Farad. Trans.* **81** (1985) 939.

Received 7 January
and accepted 13 May 1991