Redox Reaction of Nitric Oxide and Carbon Monoxide over CuO–V2O5 System

A. V. SALKER[*a], D. K. CHAKRABARTY[b] and H. V. KEER[b]

[a]Department of Chemistry, Goa University, Bambolim, Goa-403 005

[b]Department of Chemistry, Indian Insstitute of Technology, Bombay-400 076

Modern industrialisation and enormous increase of automobiles account high degree of atmospheric pollution. Transportation based on fossil fuel combustion alone is a major source of air pollution, emitting noxious gases like carbon monoxide, nitrogen oxides, unburned hydrocarbons among other species. The conversion of toxic gases into non-toxic products before discharging in the atmosphere, with suitable catalysts, is highly desired. Some countries have developed catalytic converters consisting of noble metals like platinum and platinum-palladinium alloys[1], which are not economical to the developing countries. Therefore, cheaper catalyst which can withstand high temperature and free from poisoning, is needed as substitute of the expensive automotive exhaust platinum catalyst.

Brisi and Molinari[2] reported the preparation of a variety of copper vanadates having the composition $Cu_nV_2O_{5+n}$ (where, n = 1, 2, 3, 4, 5) and Fleury[3,4] confirmed the compositions. Palanna et al.[5,6] reported their electrical and magnetic properties, and thermal studies were made by others[7,8]. In the present communication, brief studies on simultaneous oxidation-reduction of nitric oxide and carbon monoxide over $Cu_nV_2O_{5+n}$ have been reported.

Results and Discussion

The temperature dependence of NO conversion as function of catalyst temperature for different compositions is shown in Fig. 1. As the copper
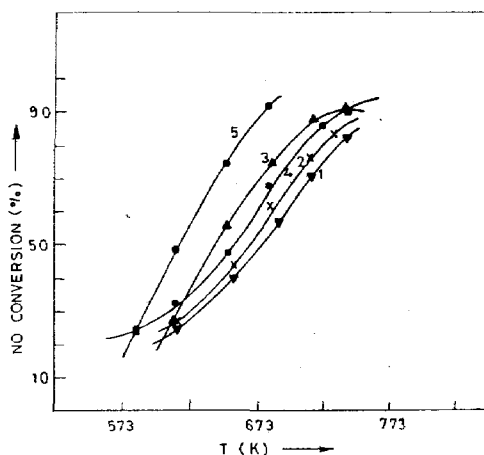

Fig. 1. Temperature dependence of NO conversion, 3×10^3 GHSV : (1) CuV_2O_6, (2) $Cu_2V_2O_7$, (3) $Cu_3V_2O_8$, (4) $Cu_4V_2O_9$ and (5) $Cu_5V_2O_{10}$.

content increases, the activity increases, except in the case of $Cu_4V_2O_9$ which showed marginally lower activity than $Cu_3V_2O_8$. $Cu_5V_2O_{10}$ showed highest activity and CuV_2O_6 the lowest. Table 1 shows the product distribution for the reduction of NO by CO over $Cu_nV_2O_{5+n}$ system. It is evident from Fig. 1 that higher the copper content, higher is the NO conversion. V_2O_5 alone is a poor catalyst for NO-CO reaction; even after activation with H_2 at 673 K for 1 h it showed poor catalytic activity. This may be so because V_2O_5 is oxygen-defficient having the formula V_2O_{5-x}, where $x = 0.01$, so that it is difficult to remove more lattice oxygen because of high binding energy. When CuO

is incorporated in V_2O_5, the binding energy decreases hence it facilitates donation of oxygen and copper ion acts as good site for NO adsorption[13].
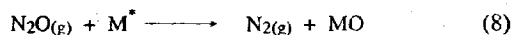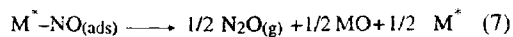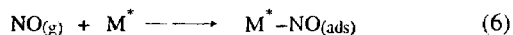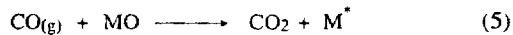
Catalyst	BET Surface area m^2g^{-1}	NO conversion %	Mole (%)		
			CO_2	N_2	N_2O
CuV_2O_6	0.52	53	61.8	31.1	7.1
$Cu_2V_2O_7$	0.75	59	62.4	30.0	7.6
$Cu_3V_2O_8$	0.54	74	62.5	31.4	6.1
$Cu_4V_2O_9$	0.68	67	62.0	29.4	8.6
$Cu_5V_2O_{10}$	0.80	92	6.43	30.6	5.1

*Inlet composition 5% NO, 5% CO in Ar, pressure, 1 atm; at 683 K catalyst temperature and 3×10^3 GHSV.

It is recognised[14] that NO adsorbs more strongly on reduced transition metal oxides than on oxidised samples. It can be adsorbed as nitrosyl with the nitrogen or the oxygen bound to the metal[15]. In addition, dissociative adsorption is found on reduced metal oxides, accompanied by oxidation of pre-reduced catalyst by NO + CO reaction, with the formation of CO_2, N_2O and N_2, the following scheme is suggested to account for the observed products :

$$2NO + V^* + 2e^- \longrightarrow N_2O + O^{2-} + V^* \qquad (1)$$

$$N_2O + V^* + 2e^- \longrightarrow N_2 + O^{2-} + V^* \qquad (2)$$

$$V^* + O^{2-} \longrightarrow VO \qquad (3)$$

$$CO + VO \longrightarrow CO_2 + V^* + 2e^- \qquad (4)$$
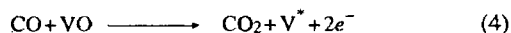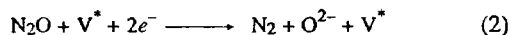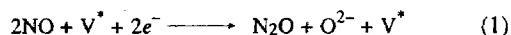
where V^* is the reduced catalyst site and VO is the oxidised catalyst site. As the temperature of the catalyst increase, higher activity is observed (Fig. 1) but the amount of N_2O in the product decreases and above 740 K only CO_2 and N_2 are the products. This shows that at higher temperature, reaction (2) is favoured.

The possible mechanism of the reduction of NO by CO over different catalysts was proposed by some investigators[1,12,13,16]. As seen from the observed products, the mechanism appears to be as follows :

$$CO_{(g)} + MO \longrightarrow CO_2 + M^* \qquad (5)$$

$$NO_{(g)} + M^* \longrightarrow M^*-NO_{(ads)} \qquad (6)$$

$$M^*-NO_{(ads)} \longrightarrow 1/2 N_2O_{(g)} + 1/2 MO + 1/2 M^* \qquad (7)$$

$$N_2O_{(g)} + M^* \longrightarrow N_{2(g)} + MO \qquad (8)$$

where, MO is the oxide catalyst material and M^* the reduced catalyst site. It is considered that the catalytic reduction of NO by CO proceeds according to a redox mechanism, with the reduction of active site being rate-controlling[12,16].

Copper vanadates were tested for studying a model NO-CO reaction and no studies were made to observed the life, poisoning and sintering effect of the catalysts. These catalysts did not show very promising activity which might be due to their low surface area.

Experimental

The compounds of compositions CuV_2O_6, $Cu_2V_2O_7$, $Cu_3V_2O_8$, $Cu_4V_2O_9$ and $Cu_5V_2O_{10}$ were prepared[2,7,9,10] by taking appropriate molar ratio of CuO and V_2O_5, mixed in an agate mortar using acetone to facilitate intimate mixing. The mixture was palletised and fired in an electric furnace, initially at 800 K for 24 h and then at 925 K for 48 h. However, the thermal treatment of the reacting oxides was varied with the composition of the constituent oxides. The products were characterised by X-ray powder diffraction technique using CuK_{α} radiation, filtered through nickel. The specific surface area of the sample was determined by the BET nitrogen adsorption method[11].

The simultaneous oxidation-reduction of reaction between NO and CO was studies in a conitnuous flow fix-bed quartz reactor, the detailed procedure being reported elsewhere[12]. The catalytic activity was determined using feed gas composition of 5% NO, 5% CO and 90% Ar. The feed gases and products were analysed by employing an on-line gas chromatograph with molecular sieve 13X and Porapak Q columns, using hydrogen as carrier gas. Each catalyst (~3 g) was taken

in the reactor to study the temperature dependence of NO conversion. Before the reaction, the catalyst was activated at 673 K in hydrogen atmosphere for ~0.5 h, then cooled down to room temperature.

References

1. R. J. H. VOORHOEVE, *Adv. Mat. Catal.*, 1977, 129.

2. C. BRISI and A. MOLINARI, *Ann. Chim.*, 1958, **48**, 263.

3. P. FLEURY, *C. R. Hebd. Scances Acad. Sci.*, 1966, **C263**, 1375.

4. P. FLEURY, *Rev. Chim. Mineral*, 1969, **6**, 819.

5. O. G. PALANNA, A. L. S. MOHAN and A. B. BISWAS, *Proc. Indian Acad. Sci.*, 1977, **86**, 455.

6. O. G. PALANNA, A. L. S. MOHAN and A. B. BISWAS, *Indian J. Phys., Sect. A*, 1979, **53**, 208.

7. R. D. SHANNON and C. CALVO, *Can. J. Chem.*, 1972, **50**, 3944.

8. A. V. SALKER, N. RAMACHANDRAN, D. K. CHAKRABARTY and H. V. KEER, "Proceedings of the 5th National Symposium of Thermal Analysis", 1985, pp. 3.32-3.34.

9. C. CALVO and D. MONOLESCU, *Acta Crystallogr. (B)*, 1973, **29**, 1743.

10. C. CALVO and R. FAGGIANI, *Acta Crystallogr. (B)*, 1975, **31**, 603.

11. J. M. THOMAS and W. J. THOMAS, "Introduction to the Principles of Heterogeneous Catalysts", Academic, London, 1967, pp. 82-86.

12. A. V. SALKER, D. K. CHAKRABARTY and H. V. KEER, *Indian J. Chem., Sect. A*, 1989, **28**, 458.

13. J. W. LONDON and A. T. BELL, *J. Catal.*, 1973, **31**, 96.

14. H. C. YAO and M. SHELEF, *J. Catal.*, 1973, **31**, 377.

15. M. SHELEX and J. T. KUMMER, *Chem. Eng. Prog.*, 1971, **67**, 74.

16. T. YONEDA, S. ITO and H. YAMAGISHI, *J. Jpn. Soc. Air Pollut.*, 1981, **16**, 88.