Mechanistic approach to NO-CO reaction over some rare earth perovskites

A V Salker

Department of Chemistry, Goa University, Goa 403206, India.

Catalytic oxidation reduction reaction between carbon monoxide (CO) and nitric oxide (NO) over perovskite type catalysts such as DyCoO₃ and SmCoO₃ have been studied from room temperature to 800 K, in a continuous flow fixed bed quartz reactor. Perovskites have been prepared by cobalticyanide method and characterized by XRD, surface area and electrical resistivity. DyCoO₃ shows higher catalytic activity than SmCoO₃. The mechanistic reaction path ways have been proposed.

Most of the environmental pollution is caused due to the combustion of fossils fuels giving out toxic gases causing serious global problems. Automobiles, factories and industrial exhausts contain harmful gases such as nitric oxide (NO), carbon monoxide (CO), hydrocarbons etc. Therefore it is essential to catalyze their conversion into non toxic products. The use of rare earth perovskites have been proposed as a possible substitute to noble metal catalysts. It has been reported that perovskites are thermally stable in exhaust environment and resistant to lead poisoning[1]. The use of perovskites in catalytic devices for the abatement of automotive exhaust emission has attracted considerable interest. The relative insensitivity of perovskites to lead and sulphur dioxide poisoning may be particularly helpful. The mechanistic understanding of NO-CO reaction depends on the availability of molecular level information regarding surface species and their role in determining overall rates and selectivity of the reaction.

Experimental

DyCoO₃ and SmCoO₃ were prepared by the cobalticynide method[2]. To the the acidified solution of MCL (M = Dy and Sm), KCo₃(CN)₆ solution was added dropwise at 360 K with constant stirring, MCo(CN)₆ thus formed were decomposed and heated at 1200 K for 12 h. A single phase compound was obtained. The simultaneous oxidation reduction of NO and CO was studied in a continuous flow, fixed bed quartz reactor, in which the weighed catalyst powder was loaded in between quartz wool plugs. An on line gas chromatograph was employed for the analysis of the reactants and the products using the molecular sieve 13x and porapak Q columns with H₂ as the carrier gas. The catalytic activity was determined using a feed gas compositions of 5% NO and 5% CO in argon (150 ml/h of NO and 150 ml/h of CO) and recording the series of chromatograms when the catalyst temperature was stabilized after 15 to 20 min. The CO was prepared by heating formic acid with conc. H₂SO₄ and NO by heating sodium nitrite with conc. H₂SO₄. These gases were further purified by passing through alkali and molecular sieve traps to remove the impurites such as carbon dioxide, nitrogen dioxide and moisture. The argon and oxygen gases were used from pure commercial cylinders. The catalysts were characterized by X-ray powder diffraction technique, BET surface area and electrical resistivity. The surface areas of the catalysts were measured by BET nitrogen adsorption method at the boiling point of liquid nitrogen.

Results and discussion

The catalysts were characterized by examining the X-ray powder diffractogrammes. The d and hkl values were found to be in agreement with the reported values. Figure 1 shows NO reduction with respect to the catalyst temperatures. The temperture dependent NO conversion showed better activity over DyCoO₃ than SmCoO₃ per unit weight. The activity increased with rise in temperature. Table 1 gives the rate and the
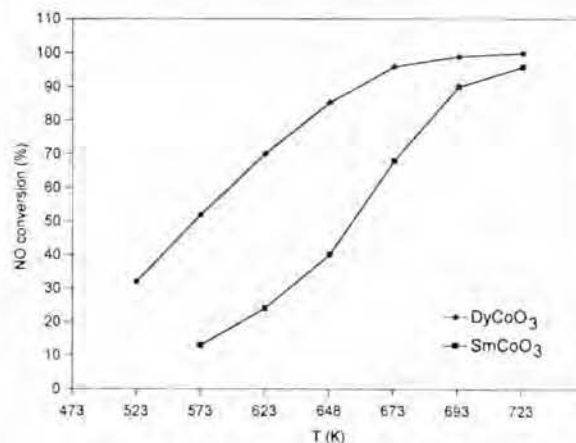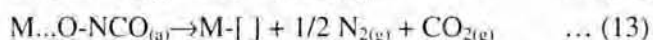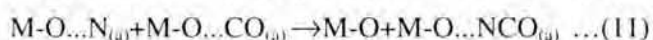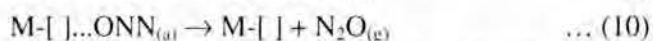

Fig. 1 — Temperature dependent NO conversion.

Table 1 — Product distribution for the reduction of NO byCO over the catalyst

Catalyst	Surface area (m²/g)	Reaction temp. (K)	NO conv. (%)	Rate (molecules/m².s)	Products formed (%)		
					N_2	CO_2	N_2O
DyCoO₃	1	573	52	2.89×10^{18}	596	38.4	2.0
SmCoO₃	0.5	573	11.2	7.80×10^{17}	71.9	22.8	5.3

product distribution for NO-CO reaction. The CO conversion for DyCoO₃ was 43% and for SmCoO₃ 9.1% at 573 K. From Table 1 it is evident that DyCoO₃ has better c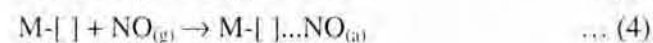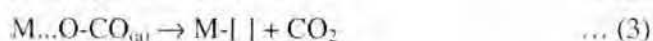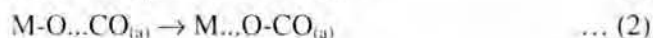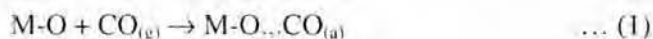atalytic activity, this may be because of higher surface area and low electrical resistivity as compared to SmCoO₃, besides high spin t_{2g} configuration for Co^{3+} which is a favourable condition for higher NO conversion rate[3].

Vibrational spectroscopy has provided evidence for adsorption of NO and CO and their adsorbate structure[4], confirming that NO - CO reaction proceeds with Langmuir Hinshelwood type mechanism. Many investigators have proposed the reaction mechanism in parts[4-7]. The reaction pathways may be represented by the following reaction steps as shown in Scheme 1.

$$M\text{-}O + CO_{(g)} \rightarrow M\text{-}O...CO_{(a)} \qquad ... (1)$$

$$M\text{-}O...CO_{(a)} \rightarrow M...O\text{-}CO_{(a)} \qquad ... (2)$$

$$M...O\text{-}CO_{(a)} \rightarrow M\text{-}[\ ] + CO_2 \qquad ... (3)$$

$$M\text{-}[\ ] + NO_{(g)} \rightarrow M\text{-}[\ ]...NO_{(a)} \qquad ... (4)$$

$$M\text{-}[\ ]...NO_{(a)} \rightarrow M...O\text{-}N_{(a)} \qquad ... (5)$$

$$M...O\text{-}N_{(a)} \rightarrow M\text{-}O...N_{(a)} \qquad ... (6)$$

$$M\text{-}O...N(a) \rightarrow M\text{-}O + 1/2\ N_{2\ (g)} \qquad ... (7)$$

$$2M...O\text{-}N_{(a)} \rightarrow M\text{-}O + M\text{-}O...NN_{(a)} \qquad ... (8)$$

$$M\text{-}O...NN_{(a)} \rightarrow M\text{-}[\ ]...O\text{-}NN_{(a)} \qquad ... (9)$$

$$M\text{-}[\ ]...ONN_{(a)} \rightarrow M\text{-}[\ ] + N_2O_{(g)} \qquad ... (10)$$

$$M\text{-}O...N_{(a)} + M\text{-}O...CO_{(a)} \rightarrow M\text{-}O + M\text{-}O...NCO_{(a)} \quad ...(11)$$

$$M\text{-}O...NCO_{(a)} \rightarrow M...O\text{-}NCO_{(a)} \qquad ... (12)$$

$$M...O\text{-}NCO_{(a)} \rightarrow M\text{-}[\ ] + 1/2\ N_{2(g)} + CO_{2(g)} \qquad ... (13)$$
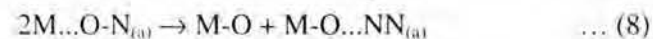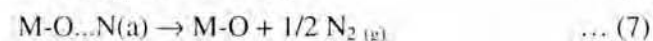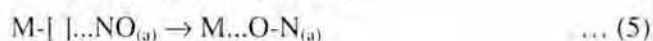
Scheme 1

Here, M-O is the oxidic perovskite catalyst site, M-[ ] is the reduced catalyst site and the subscripts (a), (g) stand for adsorbed and gas form respectively. It is observed that at lower temperature i.e. below 573 K. N_2O is also one of the products along with CO_2 and N_2. But at higher temperature i.e. above 573 K entire N_2O is reduced to N_2 and the product formed are only N_2 and CO_2 in agreement with the other results[8-10]. Therfore, at higher temperatures reactions 7, 12 and 13 are predominant than reactions 8, 9 and 10 as shown above.

Acknowledgement

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