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Catalytic Performance of Several Metallic Oxides on The Elimination Reactions of NO

by

Eiki KASAI[†], Chunbao XU^{††}, Shengli WU^{††} and Daqiang CANG^{††}**ABSTRACT**

Catalytic performance of several metallic oxides, *i.e.*, Al_2O_3 , Cu_2O , CuO , Cr_2O_3 , Fe_2O_3 , MnO_2 , Ni_2O_3 and V_2O_5 , and some of their partially-reduced samples to the elimination reaction of NO in NO-CO-CO₂-N₂ and NO-N₂ systems were examined using a flow-type reactor. The catalytic mechanism in the present condition was also discussed.

The experimental results show that most of the metallic oxide samples give a catalytic effect on NO/CO reaction with different extent. Fe_2O_3 , CuO , Ni_2O_3 and Cr_2O_3 show large catalytic activities, while those of Cu_2O , MnO_2 and Al_2O_3 are quite small. Further, it was found that the pre-reduced Ni_2O_3 sample also showed remarkable catalytic activity for direct decomposition of NO.

Key Words: metallic oxide, reduction of NO emission, catalytic activity, mechanism of catalytic reaction, direct decomposition of NO

1. Introduction

It is well known that nitrogen oxides (NO_x) are not only harmful to human being, but also major causes of acid rain and greenhouse effect which damage ecology and environment in the global scale¹⁾. With the rapid development of industry and transportation systems, NO_x emission from combustion process of fossil fuels significantly increases and results to more severer pollution, *e.g.*, acid rain in European countries and north America. Therefore, reduction of NO_x emission becomes to one of the urgent issues of the world.

Just as coal-firing power plants and automobile engines, ironmaking process is a major emission source of NO_x. Especially, the sintering process of iron ores discharges nearly 50% of the total NO_x emission in the ironmaking industries in Japan. Because of a large volume of exhaust gas formed from the iron-ore sintering process, the cost of flue gas de-NO_x is quite high. Therefore, great efforts have been made to develop "in-situ reduction of NO_x" which realizes suppression of NO_x formation and/or elimination of NO_x within the processes²⁾⁻⁵⁾. The authors⁶⁾⁻⁸⁾ have reported the effects of fuel (coke granule) types with different adhering materials, *i.e.*, Fe_2O_3 , Fe_3O_4 , FeO , Fe , SiO_2 , Al_2O_3 , $\text{Ca}(\text{OH})_2$, CaSO_4 and their mixtures, on the formation of NO_x during combustion in

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packed beds. They showed that use of not only lower oxides of iron, *i.e.*, magnetite (Fe_3O_4) and wustite (FeO), but also hematite (Fe_2O_3) and calcium ferrites ($n\text{CaO} \cdot m\text{Fe}_2\text{O}_3$) can reduce NO_x emission. In such case, NO/CO reaction seems to play a significant role and this may be important to improve *in-situ* suppression reactions of NO_x during the combustion processes of fossil fuels.

On the basis of such results, the catalytic phenomena of various metallic oxides (Al_2O_3 , Cu_2O , CuO , Cr_2O_3 , Fe_2O_3 , MnO_2 , Ni_2O_3 and V_2O_5) and some of their partially-reduced samples for the elimination reactions of NO was examined in the present study. At the same time, their catalytic mechanism in $\text{NO}-\text{CO}-\text{CO}_2-\text{N}_2$ and $\text{NO}-\text{N}_2$ systems was discussed.

2. Experimental

2.1 Sample Preparation

Metallic oxide samples, *i.e.*, Al_2O_3 , Cu_2O , CuO , Cr_2O_3 , Fe_2O_3 , MnO_2 , Ni_2O_3 and V_2O_5 , used in the experiment are fairly pure (impurities are less than 0.5 mass% in total) powder reagents. They were weighed and mixed well with the addition of a certain amount of distilled water, and then granulated to form spherical particles having diameters between 3 and 4 mm. Prepared granules were dried at 100°C for 1 hour and gradually heated up to 800°C , and hold at this temperature in air for 3 hours. The obtained granules were subjected to the following experiments.

2.2 Experimental Apparatus and Procedure

The experimental apparatus is schematically shown in Fig. 1. The reactor was made of alumina tube (inside diameter : 30 mm, length : 500 mm). In order to preheat and distribute well the introduced gas, alumina spheres of 2 to 3 mm diameter were packed in the lower part with 30 mm height. Sample bed with 15 mm height was placed on the alumina sphere bed. Pure N_2 gas was flowed through beds during heating up to an experimental temperature and then the gas was changed

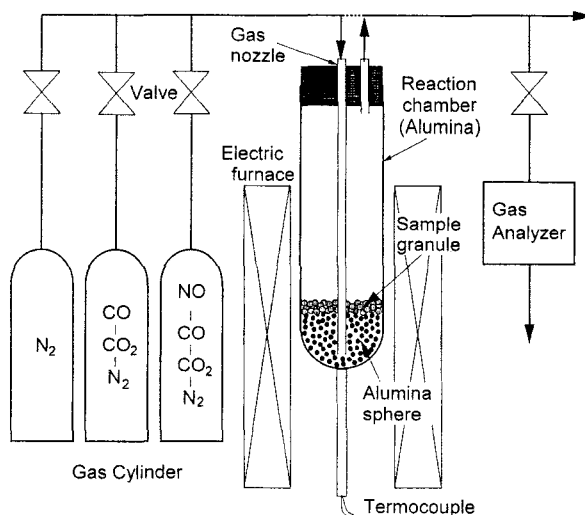


Fig. 1 Schematic diagram of experimental apparatus.

to a specified gas mixture. Introduced gases were prepared by mixing pure gases to have a certain composition. The gas mixture was introduced to the reactor with a flow rate of $1400 \text{ Ncm}^3/\text{min}$. Concentration of NO in the outlet gas was continuously measured by an infrared NO analyzer.

3. Results

3.1 Reaction without Metallic Oxide Sample (Blank Test)

As a blank test, the gas mixture of 800 ppm NO - 0.2% CO - 2.0% CO₂ - N₂ was made to flow through only the alumina sphere bed preheated at different temperatures without metallic oxide sample in the reactor. Changes in NO concentration in outlet gas with preheating temperature is shown in Fig. 2. The figure shows that the NO/CO reaction both on the surface of the alumina spheres and as a homogeneous reaction is very slow at any temperature, and the maximum conversion ratio of NO is only 3%. Such results are well consisted with the results of previous studies^{4, 7}.

3.2 Catalytic Effect of Metallic Oxide Samples

Figure 3 shows change in NO concentration in outlet gas with time after the gas mixture of 800 ppm NO - 0.2% CO - 2.0% CO₂ - N₂ flows through the bed of different metallic oxide samples at 500°C. All the curves give similar trends: NO concentration decreases in the early stage and reaches stable values after a certain period.

The conversion ratio of NO (CR) was defined as follows:

$$\text{CR} (\%) = \left(\frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \right) \times 100 \quad (1)$$

where $[\text{NO}]_{\text{inlet}}$ and $[\text{NO}]_{\text{outlet}}$ are concentration of NO (ppm) in inlet and outlet gases, respectively. The CR when concentration of NO in outlet gas reaches a lower stable value is called as the stable conversion ratio (SCR). Therefore, SCR represents catalytic ability of metallic oxide samples for

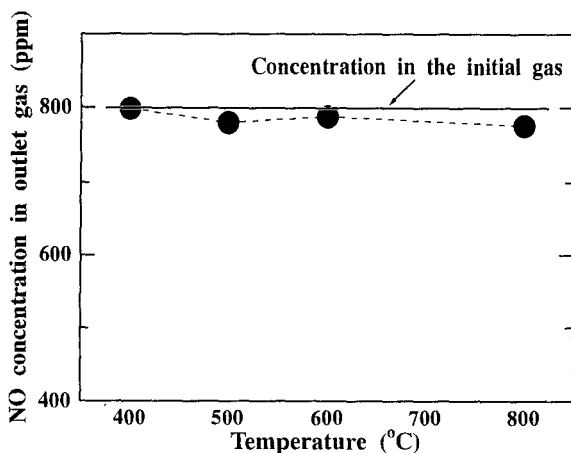


Fig. 2. Concentration of NO in the outlet gas measured by the blank test.

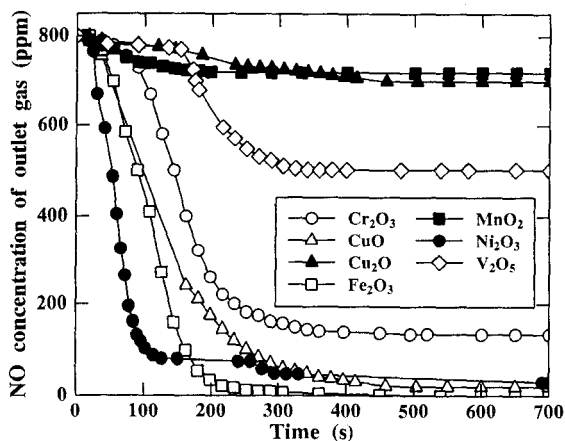


Fig. 3. Changes in NO concentration in outlet gas with time measured at 500°C for different metallic oxide samples.

the reactions of NO elimination. The values of SCR obtained for the samples are listed in Table 1.

Table 1. SCR values obtained for the metallic oxide samples at the preheating temperature 500°C.

Samples	Al ₂ O ₃	Cu ₂ O	MnO ₂	Cr ₂ O ₃	V ₂ O ₅	Fe ₂ O ₃	CuO	Ni ₂ O ₃
SCR(%)	2.5	12.5	11.3	83.1	37.0	100.0	97.5	98.1

CuO, Cr₂O₃, Fe₂O₃ and Ni₂O₃ show large SCR values. In terms of SCR, the order of catalytic activity of used metallic oxide samples in the 800 ppm NO - 0.2% CO - 2.0% CO₂ - N₂ system at 500°C is: Fe₂O₃ > CuO > Ni₂O₃ > Cr₂O₃ > V₂O₅ > Cu₂O > MnO₂ > Al₂O₃. From Fig. 3, there is an "induction period" in the initial stage of reaction where NO concentration in outlet gas does not change. This may be due to a complex mechanism of gas-solid reaction which includes the adsorption of reactant-gas molecules on the surface of metallic oxide, the mutual effect of reactant-gas molecules and active spots on the surface of metallic oxide, the desorption of reacted molecules from the surface and the change of oxidation state and/or the structure in the surface and the bulk of metallic oxide. Different sample gives different induction period and it is worthy to note that the induction period of any metallic oxide at 800°C is shorter than that at 500°C. At present, there are very few studies on such mechanism, and further researches are required.

Table 2. SCR values obtained for the metallic oxide samples at the preheating temperature 800°C.

Samples	Al ₂ O ₃	Cu ₂ O	Cr ₂ O ₃	Fe ₂ O ₃	CuO	Ni ₂ O ₃
SCR(%)	3.0	93.8	99.6	96.3	95.0	99.9

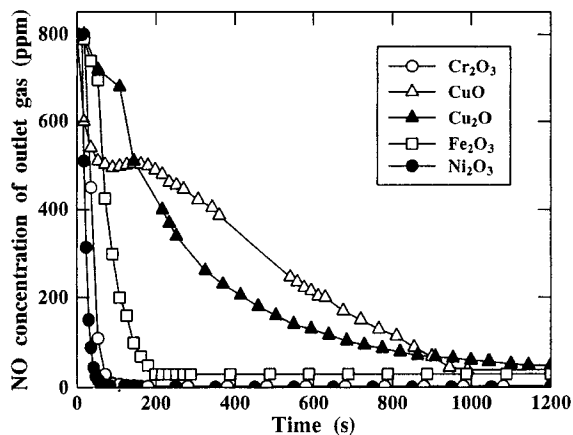
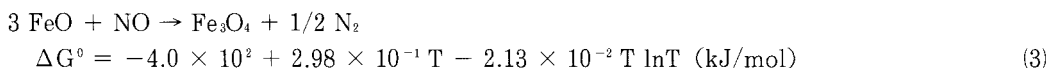
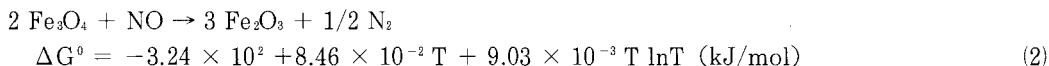


Fig. 4. Changes in NO concentration in outlet gas with time measured at 800°C for different metallic oxide samples.

The results obtained at 800°C are shown in Fig. 4 and SCR values obtained are given in Table 2. Comparing Figs. 3 with 4, it is clear that reaction temperature gives large effect on the catalytic activity. In term of SCR, the catalytic activities of Cu_2O , Cr_2O_3 and Ni_2O_3 at 800°C are considerably higher than 500°C, and those of CuO and Fe_2O_3 at 800°C are little lower than 500°C. Generally, the reactions (including decomposition of reactants) on the surface of metallic oxides is a rate-limiting step of the overall catalytic reaction in gaseous systems. Therefore, the overall reaction rate normally becomes faster with an increase in temperature. However, in the case that adsorption of reactant-gas molecules is a rate limiting step, the overall reaction rate may decrease with increasing temperature. Further, surface area of samples may be decreased by a change of their structure, *e.g.*, surface roughness and porosity, at high temperature due to a sintering effect.

4. Discussion

Possible explanation for reactions of NO elimination in the system of $\text{NO-CO-CO}_2\text{-N}_2$, is summarized in Fig. 5. The experimental result (see Fig. 2) shows that homogeneous reaction between NO and CO occurs but is not important. Metallic oxides can be reduced to the lower oxides by CO in the system and then NO reduced by them⁷⁾. For example, the reaction between iron-oxides and NO can be described as Eqs. (2) and (3).



In order to investigate this phenomena in detail, following experiments were conducted: several metallic oxide samples, *i.e.*, CuO , Cu_2O , Cr_2O_3 , Fe_2O_3 and Ni_2O_3 , were partially pre-reduced at certain temperature for 20 min with flow of gas mixture of 0.2% CO - 2% CO_2 - N_2 and then gas was changed to 800ppm NO - N_2 . Figure 6 shows the results at 800°C. CuO , Cu_2O , Cr_2O_3 and Fe_2O_3 indicate simi-

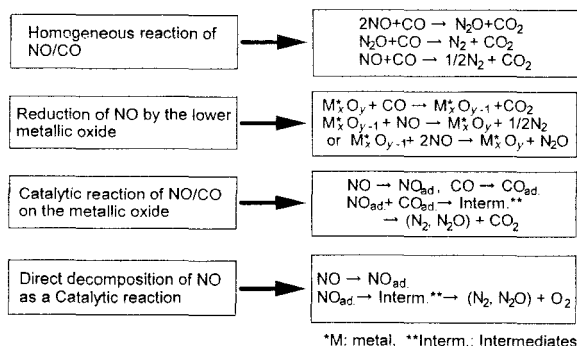


Fig. 5. Possible paths of the elimination reaction of NO in the present system.

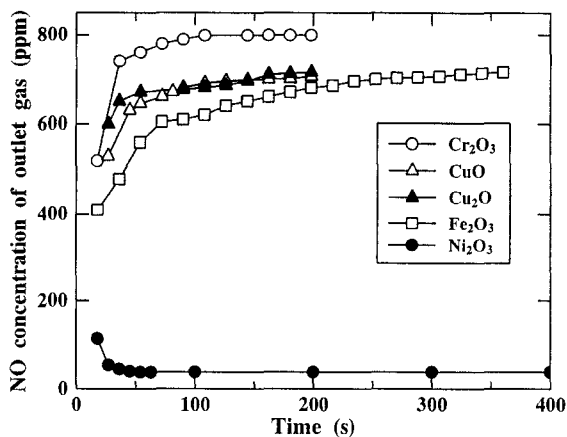


Fig. 6. Changes in NO concentration in outlet gas with time measured at 800°C for prereduced samples.

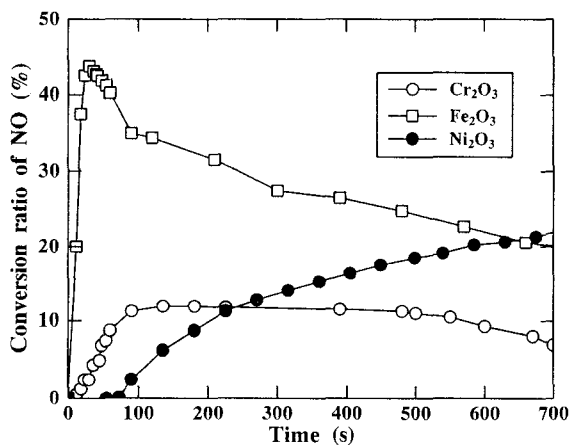


Fig. 7. Changes in conversion ratio NO obtained at 500°C for some metallic oxide samples.

lar trends that NO concentration increases with time. It could be interpreted that the reduction ability of the samples decreases as the lower oxides are oxidized. However, NO concentration curve for the pre-reduced Ni₂O₃ sample shows extremely different feature from those for the other samples. NO concentration does not increase but decreases continuously with prolonged time. After about 50 s, NO concentration reaches a stable value with a high SCR value as much as 95%. Such remarkable phenomenon is quite interesting but difficult to clearly explain in terms of only the reduction of NO by the lower oxide. However, it is possible to point out that the pre-reduced Ni₂O₃ would give a remarkable effect on direct decomposition of NO.

Previous reports⁹⁻¹⁰⁾ have stated that some metallic oxides have certain catalytic effects on the direct decomposition of NO. In order to investigate such effects, gas mixture of 800 ppm NO-N₂ was introduced to the packed bed of Fe₂O₃, Ni₂O₃ and Cr₂O₃ samples without pre-reduction. Figure 7 shows the changes in NO conversion ratio with time at 500°C. Every metallic oxide sample shows a certain catalytic effect, although values of CR for Fe₂O₃ and Cr₂O₃ lower with prolonged time. However, CR for Ni₂O₃ sample continuously increases and it is a similar tendency to its pre-reduced sample (see Fig. 6). Considering the above results, it can be seen that the catalytic effect on the NO/CO reaction plays a leading role in the NO-CO-CO₂-N₂ system for most of the metallic oxide samples but direct decomposition of NO may significantly occur on a few oxides.

At present, the mechanism and pathway for the catalytic reaction of NO/CO is not perfectly known. Both N₂O¹¹⁻¹³⁾ and NCO¹⁴⁻¹⁵⁾ have been regarded as intermediate in the reaction. It is called as "redox mechanism" (metallic oxides on the surface being reduced and oxidized cyclically)¹⁶⁻¹⁷⁾. According to this mechanism, the catalytic activity of metallic oxides may relate to their free energy of formation. The lower free energy of formation will lead to stronger the bond and it is therefore difficult to be reduced by CO and consequently has lower catalytic activity. Figure 8 indicates the relation between SCR obtained by the gas mixture of 800 ppm NO - 0.2% CO - 2.0% CO₂

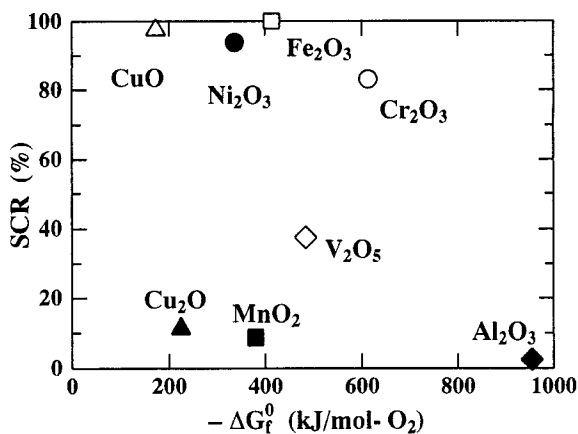


Fig. 8. Changes in NO concentration in outlet gas with time measured at 800°C for prerduced samples.

-N₂ at 500°C for the metallic samples without pre-reduction and their free energy of formation. Although the metallic oxide samples may be sorted as the high SCR (more than 80%) group, *i.e.*, CuO, Ni₂O₃, Fe₂O₃ and Cr₂O₃, and the others, *i.e.*, Cu₂O, MnO₂, Al₂O₃ and V₂O₅, no clear relation can be seen between SCR and the corresponding free energy of formation. Free energy gives, of course, only information in an equilibrium condition. Further studies such as *in-situ* analyses of the oxide surface and adsorbed gases are needed to understanding the mechanism in detail.

5. Conclusions

Catalytic performance of several metallic oxides, *i.e.*, Al₂O₃, Cu₂O, CuO, Cr₂O₃, Fe₂O₃, MnO₂, Ni₂O₃ and V₂O₅, and some of their partially-reduced samples to the elimination reaction of NO was examined using a flow-type reactor. The results are summarized as follows:

- (1) In the NO-CO-CO₂-N₂ system, all metallic oxide samples used in the experiment show certain catalytic activities on the elimination reaction of NO to different extent. The order of catalytic activity is Fe₂O₃ > CuO > Ni₂O₃ > Cr₂O₃ > V₂O₅ > Cu₂O > MnO₂ > Al₂O₃ at 500°C.
- (2) Temperature influences the catalytic activity of the metallic oxides. The catalytic activities of Cr₂O₃ and Cu₂O at 800°C are significantly larger than those at 500°C.
- (3) An "induction period" was observed for the elimination reaction of NO with metallic oxides samples in the NO-CO-CO₂-N₂ system and it shortened with increase in the preheating temperature.
- (4) Pre-reduced nickel oxide sample remarkably promotes the direct decomposition of NO.

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