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The Catalytic Reduction of Nitric Oxide by Carbon Monoxide over a Fe_2O_3 Catalyst

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Synopsis. When nitric oxide was admitted during the course of the reduction of N_2O by CO, a discontinuous increase in the N_2O pressure and a decrease in the NO pressure were observed. The reduction of N_2O stopped completely, and only the reduction of NO to N_2O proceeded.

Earlier papers[1-5] have noted the appearance of N_2O as an intermediate in the catalytic reduction of NO by CO. High activity at low temperatures and low N_2O formation are desirable properties of the catalyst for the removal of NO from stack gas. However, the fundamental aspects of the N_2O formation still remain ambiguous. Fe_2O_3 is one of the catalysts over which the N_2O formation is most prominent.[2] We wish to investigate the catalytic reduction of NO by CO over a Fe_2O_3 catalyst in a closed circulating system, in order to obtain more detailed information relating to the appearance of N_2O in the gas phase.

Experimental

The apparatus employed is a closed circulating system, the total volume of which is 861 ml.

The Fe_2O_3 catalyst was prepared by impregnating silicon carbide, pulverized into 14—30 mesh, with a $Fe(NO_3)_3$ solution. The catalyst thus obtained was dried at 110 °C and then calcined at 500 °C for 5 hr. The metal content was 10 wt% as Fe_2O_3, and its total surface area was 2.40 m^2/g.

Before initiating the experimental runs, the catalyst was degassed at 350 °C for 1 hr and was then treated with a mixture of NO and CO in the same composition, or with the same combination of N_2O and CO as that used for the reaction runs, and at the same temperatures. This procedure allowed us to obtain a good reproducibility in a series of experiments. The experimental runs were carried out at such circulating velocities of gasses that the reaction rate was not affected.

The analyses of the reactant and the product were conducted using a series of two gas-chromatographic apparatuses equipped with thermoconductivity detectors. The first apparatus was operated at 80 °C, using a stainless steel column (3 mm × 1 m) packed with Unipack 1A (60—80 mesh) obtained from Gasukuro Kogyo, Tokyo, for the N_2O and CO_2 separations. The second apparatus was operated at 60 °C, using a stainless steel Column (3 mm × 2 m) packed with Molecular Sieve 13X (60—80 mesh), for the N_2, NO, and CO separations. Helium was used as a carrier gas. The reproducibility of each component was within 0.3 Torr.

Results and Discussion

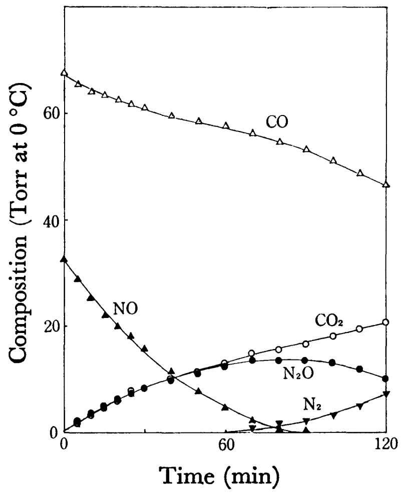

Fig. 1. The reduction of NO over 5 g of 10 wt% Fe_2O_3 on silicon carbide at 200 °C.

Figure 1 shows a typical result of the reduction o NO by CO over a Fe_2O_3 catalyst at 200 °C. Only the partial reduction of NO to N_2O took place at an early stage, and the reduction of N_2O to N_2 occurred after most of the NO had been consumed. At such a high temperature as 300 °C, a small amount of N_2 was produced even at an early stage, but the reduction of NO to N_2O was still dominant.† The initial rates of the reduction of N_2O to N_2 by CO in the absence of NO were comparable with those of NO to N_2O. We are, therefore, interested in the selective formation of N_2O in the reduction of NO by CO. Previous workers[1-4] using the flow system also observed N_2O formation in the reduction of NO by CO at low temperatures or at high space velocities, but little attention has been paid to the reasons why NO reduces to N_2O selectively and why scarcely reduction of the N_2O formed on the catalyst proceeds. Therefore, it is of interest to investigate the perturbation effect of NO on the reduction of N_2O by CO; NO was admitted during the course of the reduction of N_2O, as is shown in Fig. 2. A discontinuous increase in the N_2O pressure and a decrease in the NO pressure were observed upon the introduction of NO at a certain time, *A*. However, the CO and CO_2 pressures were changed continuously. Moreover, the reduction of N_2O and the N_2 formation stopped completely, and the reduction of NO to N_2O occurred. A similar effect of NO was also observed at 250 °C, although a slight formation of N_2 was found.

The following reaction schemes are generally accepted for the reduction of NO by CO:[1-4]

$$CO + cat \xrightarrow{k_1} CO_2 + cat^* \qquad (1)$$

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† No decomposition of NO to N_2O and O_2, or of N_2O to N_2 and O_2, in the absence of CO was observed under our conditions.

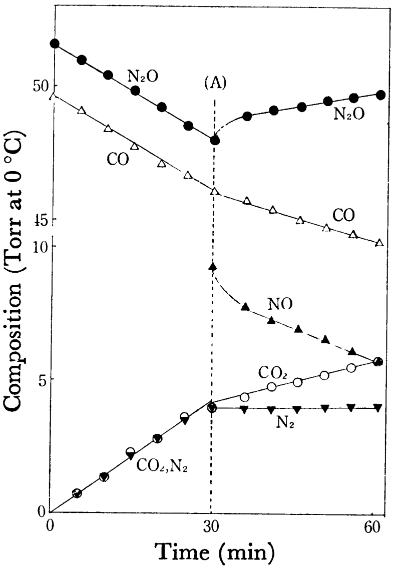

Fig. 2. The effect of NO on the reduction of N_2O by CO over 2 g of 10 wt% Fe_2O_3 on silicon carbide at 200 °C. NO (9.2 Torr) was introduced at a time *A*.

$$2NO + cat^* \xrightarrow{k_2} N_2O + cat \qquad (2)$$

$$N_2O + cat^* \xrightarrow{k_3} N_2 + cat \qquad (3)$$

where cat and cat* are an active site on the catalyst and its reduced site by CO respectively, and where k_1, k_2, and k_3 are the rate constants for each reaction. If the selective formation of N_2O is due to $k_2 \gg k_3$ (the last step may be rate-limiting), the introduction of NO during the course of the reduction of N_2O should result in the enhancement of the N_2 formation, because the concentration of N_2O on the catalyst should increase. Therefore, our results cannot be explained by the difference in rate constants, but must be related to the strong adsorption of NO on the catalyst.

Our results do not permit any definitive descriptions of the selective formation of N_2O in the reduction of NO by CO, but we have adopted the one presented below as a tentative postulate. The selective formation of N_2O observed at an early stage of the reduction of NO reflects the difference in adsorptivity between NO and N_2O: the adsorption of NO is stronger than that of N_2O. The NO and N_2O formed on the catalyst will establish an adsorption equilibrium, and the N_2O is displaced by NO before it is converted to N_2. As the temperature is raised, a part of the N_2O formed on the catalyst will be reduced to N_2 before the displacement by NO. The effect of NO on the reduction of N_2O shown in Fig. 2 also supports the above postulate: the discontinuous increase in N_2O pressure and the stopping of the N_2 formation may be ascribed to the displacement of N_2O by NO.

References

1) R. A. Baker and R. C. Doerr, *Ind. Eng. Chem., Process Des. Develop.*, **4**, 188 (1965).

2) M. Shelef and K. Otto, *J. Catal.*, **10**, 408 (1968).

3) M. Shelef, K. Otto, and H. Gandhi, *ibid.*, **12**, 361 (1968).

4) G. L. Bauerle, G. R. Service, and K. Nobe, *Ind. Eng. Chem., Prod. Research Develop.*, **11**, 54 (1972).

5) J. W. London and T. Bell, *J. Catal.*, **31**, 96 (1973).