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ENHANCEMENT OF CATALYTIC ACTIVITY OF ALUMINA BY COPPER ADDITION FOR SELECTIVE REDUCTION OF NITROGEN MONOXIDE BY ETHENE IN OXIDIZING ATMOSPHERE

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The catalytic activity of alumina for the title reaction has been found to be greatly improved by the loading of copper. The addition of copper resulted in lowering the active temperature region, the higher maximum activity, and the enhancement of the reaction rate. The maximum effect was observed at 0.3 wt% of the loading amount of copper. A similar enhancement was also confirmed on SiO_2-Al_2O_3.

Keywords: Nitrogen monoxide, selective reduction, copper, alumina, silica-alumina

1. Introduction

The selective reduction of nitrogen monoxide (NO) by hydrocarbons such as C_2H_4, C_3H_6, and C_3H_8 in an oxidizing atmosphere has been reported over several catalysts [1–6]. This new type of reduction of NO has recently been found to proceed even in the presence of SO_2 [7]. There is the possibility that this might overcome the disadvantages or problems of the present reduction systems using dangerous and expensive ammonia. Among the active catalysts for the reaction, alumina reported by Hamada et al. [5] would be strong candidate for the practical catalyst, since alumina is one of the widely used, cheap, and heat-stable catalysts or supports. However, the active temperature was much higher than that of the emission gas from diesel engine (473–673 K) and the activity was still low. In this study we have investigated additive effect of various elements on the catalytic activity of alumina and silica-alumina. We wish to report that copper, cobalt, or iron is effective to enhance the catalytic activity and that the additive effect of copper is observed not only on alumina but also on silica-alumina.

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2. Experimental

Al_2O_3 (JRC-ALO 4) and SiO_2-Al_2O_3 were obtained from Catalysis Society of Japan and Catalysts & Chemicals Ind. Co., respectively. The metal-loaded catalysts were prepared by impregnation of the oxides to incipient wetness with aqueous solution of metal nitrates. Then the samples were calcined at 823 K for 4 h. The catalytic reduction of NO was carried out with a fixed bed flow reactor. The reactant gas contained 1000 ppm of NO, 250 or 1000 ppm of C_2H_4, and 2% of O_2. Total flow rate was 80–200 $cm^3 \cdot min^{-1}$ and the catalyst weight was 0.1–0.7 g. The catalytic activity for NO removal was evaluated by the extent of conversion into N_2.

3. Results and discussion

The catalytic activity of alumina was greatly changed upon only 0.2 wt% loading of various metals. The metals used in the present study have been classified into three groups; the elements promoting the activity, showing little effect, and decreasing the activity. The results are shown in figs. 1(a), (b), and (c). It is clear that the activity of Al_2O_3 at the temperatures of 573–773 K was enhanced by adding Cu, Fe, Co, or Cr, while Ni, Mn, Zn, and V little affected the activity and the activity was decreased by adding Ag, Ca, and K. It should be noted in the first group that copper, cobalt, and iron (or chromium) lowered the active temperature region of Al_2O_3 and the first two metals increased the maximum catalytic activity of Al_2O_3. It follows that copper is one of the best additives to enhance the catalytic activity of alumina for the selective reduction of NO with ethene in an oxidizing atmosphere.

Clearly the most active temperatures are depending on the cations supported. The order of active temperature regions was Fe (the most active temperature, 673 K) $\approx$ Cr (673 K) $<$ Cu (723 K) $<$ Co (773 K) $\leq$ Ni (773–823 K) $\leq$ Mn (823 K) $\approx$ V (823 K) $\approx$ Zn (823 K) $\approx$ K (823 K) $\approx$ none (Al_2O_3 only, 823 K) $<$ Ag (873 K) $\approx$ Ca (873 K).

The activity of Cu/Al_2O_3 depended on the loading amount of copper; the dependency is shown in fig. 2. The activity at 723 K was much increased by adding a small amount of copper (0.1 wt%) onto Al_2O_3, reached maximum at the loading amount of 0.3 wt%, and then decreased at higher loading levels. A similar dependence of the activity on the loading amount of copper was observed at the reaction temperature of 673 K.

The correlation between the catalytic activity of 0.2 wt% Cu/Al_2O_3 or Al_2O_3 and space velocity is shown in fig. 3. The reaction temperature was set at their active temperature, 773 K. The activity of Al_2O_3 greatly decreased in the GHSV region of 4500–45000 h^{-1}. By contrast, Cu/Al_2O_3 showed a characteristic dependency on GHSV. The conversion into N_2 did not change below 9000 h^{-1}

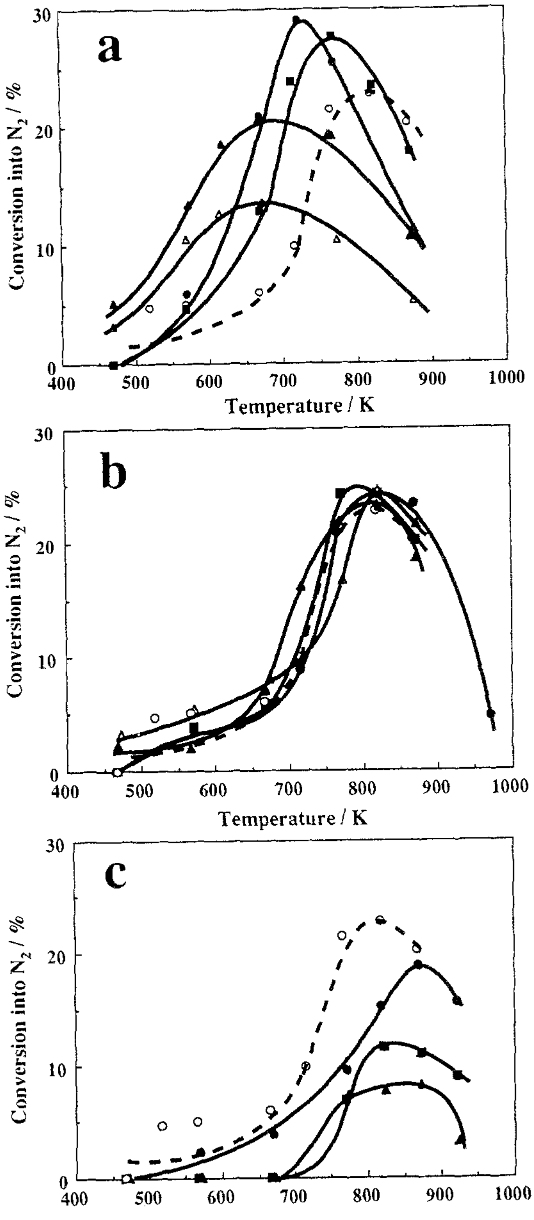

Fig. 1. Temperature dependence of the catalytic activities of various metal-loaded alumina. Catalyst weight, 0.5 g. NO (1000 ppm), C_2H_4 (250 ppm), and O_2 (2%). Total flow rate, 150 $cm^3 \cdot min^{-1}$. The loading amount of metals, 0.2 wt%. Fig. 1a: ●, Cu; ■, Co; ▲, Fe; △, Cr. Fig. 1b: ■, Ni; ▲, Mn; ●, Zn; △, V. Fig. 1c: ●, Ag; ■, K; ▲, Ca. ○— — —○ in figs. 1a–1c indicate the activity of Al_2O_3.

and gradually decreased at higher GHSV region. The results again indicate that the copper is an excellent additive to improve the activity of Al_2O_3 for the selective reduction of NO.

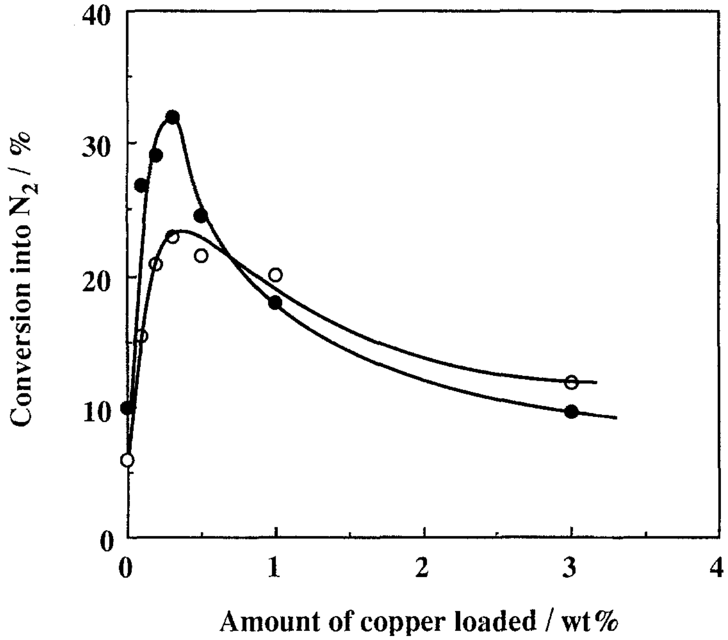

Fig. 2. Dependence of the activity of Cu/Al_2O_3 on the loading amount of copper. Catalyst weight, 0.5 g. NO (1000 ppm), C_2H_4 (250 ppm), and O_2 (2%). Total flow rate, 150 $cm^3 \cdot min^{-1}$. ○, 673 K; ●, 723 K.

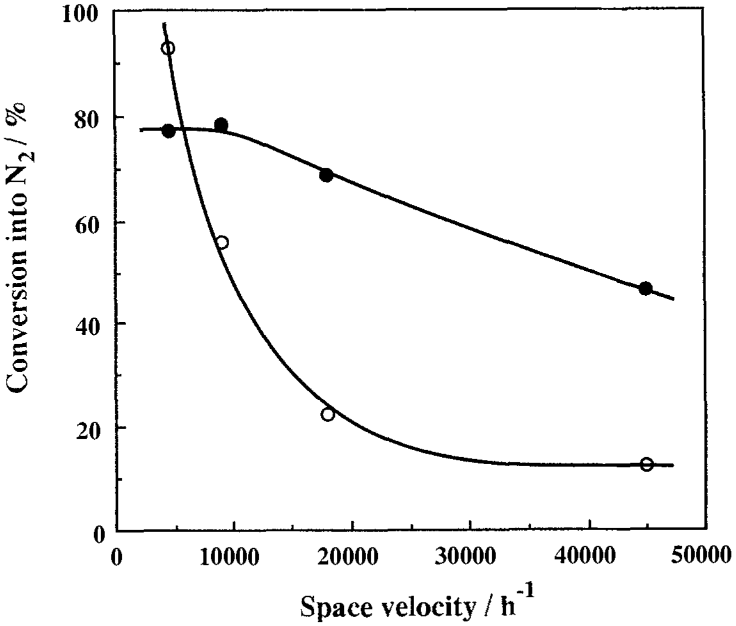

Fig. 3. Correlation between the catalytic activities and space velocity. Catalyst weight; 0.1–0.7 g. Total flow rate, 80–200 $cm^3 \cdot min^{-1}$. Reaction temperature, 773 K. NO (1000 ppm), C_2H_4 (1000 ppm), and O_2 (2%). ●, Cu (0.2 wt%)/Al_2O_3; ○, Al_2O_3.

Copper also promoted the activity of SiO_2-Al_2O_3. The activities of SiO_2-Al_2O_3 for the selective reduction of NO at the temperatures of 573–873 K was increased by a factor of 3–5 when 3.3 wt% copper was added. For example, the conversion into N_2 was increased from 9% to 31% at 773 K in a NO (1000 ppm) + C_2H_4 (250 ppm) + O_2 (2%) system: The latter value is comparable to that on Cu/Al_2O_3.

Next, we briefly discuss the reaction mechanism. At present three kinds of reaction schemes can be proposed; (1) decomposition of NO proceeds to yield N_2 and then the hydrocarbon clean up the surface oxygen [8], (2) some reaction intermediates formed in the oxidation of the hydrocarbon have ability to reduce NO selectively, and (3) NO_2 generated from NO and O_2 can preferentially react with the hydrocarbon. Taking into consideration that the presence of oxygen is essential to promote the selective catalytic reduction [1,2,6,9], the reaction (2) or (3) would be appropriate. Further spectroscopic studies to elucidate the mechanism are in progress.

In conclusion, copper is clarified to be an excellent additive to improve the catalytic activity of Al_2O_3 and SiO_2-Al_2O_3 at the temperatures as low as 573–773 K for the selective reduction of NO by ethene in an oxidizing atmosphere.

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