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A Remarkable Increment in Catalytic Activity of SiO_2-Al_2O_3 by Copper Addition for Selective Reduction of Nitrogen Monoxide by Ethene in Oxidizing Atmosphere

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The addition of 3.3-3.7 wt% copper resulted in the great increment in the catalytic activity of the parent SiO_2-Al_2O_3 for the title reaction in the wide temperature region 573-900 K.

The selective reduction of nitrogen monoxide (NO) by hydrocarbons in an oxidizing atmosphere has been reported over copper ion-,[1,2] proton-,[3] or cerium ion-[4] exchanged zeolites, alumina, and silica-alumina,[5,6] and Fe-silicate[7] catalysts. Among the support materials, alumina or silica-alumina reported by Hamada et al.[5] would be a strong candidate for the practical catalyst, since these oxides are one of the widely used, cheap, and thermally stable catalysts or supports. Recently, we have found that the addition of copper onto Al_2O_3 resulted in lowering the active temperature region and the enhancement of reaction rate.[6] On the other hand, the catalysts having wider active temperature region is desired from the practical point of view because of the variation of the temperature of real exhaust gases. Here we wish to report that the addition of copper greatly enhanced the catalytic activity of SiO_2-Al_2O_3 in the temperature region as wide as 573-900 K.

SiO_2-Al_2O_3 with an Al_2O_3 content of 28.6 wt% was obtained from Catalysts & Chemicals Ind. Co. Cu/SiO_2-Al_2O_3 were prepared by an ion exchange using an aqueous solution of copper(II) nitrate with (Cu content $\geq$ 3.7 wt%) or without (Cu content $\leq$ 3.3 wt%) ammonia addition. The achievement of higher content of Cu on SiO_2-Al_2O_3 by ammonia addition is probably due to the exchange between H^+ and $Cu_2(OH)^{3+}$, $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$, or $Cu_3(OH)_2^{4+}$ formed at specific pH.[8] The solid was collected and then dried at 353 K overnight. Just before the reaction, the samples were treated in a He stream at 773 K for 2 h. The catalytic reduction of NO was carried out with a fixed bed flow reactor. The reactant gas contained 1000 ppm of NO, 250 ppm of C_2H_4, and 2% of O_2. Total flow rate was 150 $cm^3 \cdot min^{-1}$ and the catalyst weight was 0.5 g. The catalytic activity for NO removal was evaluated by the extent of conversion into N_2.

The conversion of NO on Cu(3.3 wt% as metal)/SiO_2-Al_2O_3 did not change when the reaction temperature was raised and lowered stepwise between 773 and 973 K, showing that the catalyst was not deactivated in the present condition. The effect of copper loading on SiO_2-Al_2O_3 is shown in Fig. 1A. If one compares the data of the symbols ● and ❐ in Fig. 1A, it is clear that the addition of 3.3 wt% copper much improved the catalytic activity of SiO_2-Al_2O_3 as follows: (1) The maximum activity was increased by a factor of about two at 9000 h^{-1}. Such an increment of the maximum catalytic activity for the selective reduction of NO by the additives at low SV has not been reported except for Co/SiO_2.[9] (2) In the reaction temperature range as wide as 573-900 K, the activity of

SiO_2-Al_2O_3 was increased; for example, Cu(3.3 wt%)/SiO_2-Al_2O_3 was active in a wide temperature region 673-873 K.

The conversions into N_2 and of C_2H_4 on Cu/SiO_2-Al_2O_3 depended on the amount of copper loaded as shown in Figs. 1A and 1B, respectively. When 1.3 wt% of copper was added on SiO_2-Al_2O_3, the conversion into N_2 was most increased around 873 K. The addition of 3.3 wt% copper increased the conversion into N_2 in the whole range of 673-873 K. The loading of 3.7 wt% copper greatly increased the conversion into N_2 around 600 K, though the conversion into N_2 around 873 K was slightly decreased. Further addition of copper decreased the conversions into N_2 around 600 K and 873 K. On the other hand, Fig. 1B indicates that the activity of Cu/SiO_2-Al_2O_3 catalysts for the C_2H_4 oxidation is roughly dependent on the content of copper. For example, above 600 K C_2H_4 was almost consumed on Cu/SiO_2-Al_2O_3 having the loading amount of copper above 5.7 wt%. The results in the figures suggest that the activity for the conversion into N_2 is related to the ability of the catalyst for oxidation of C_2H_4 by oxygen or NO and that too much oxidation ability would result in low conversions into N_2.

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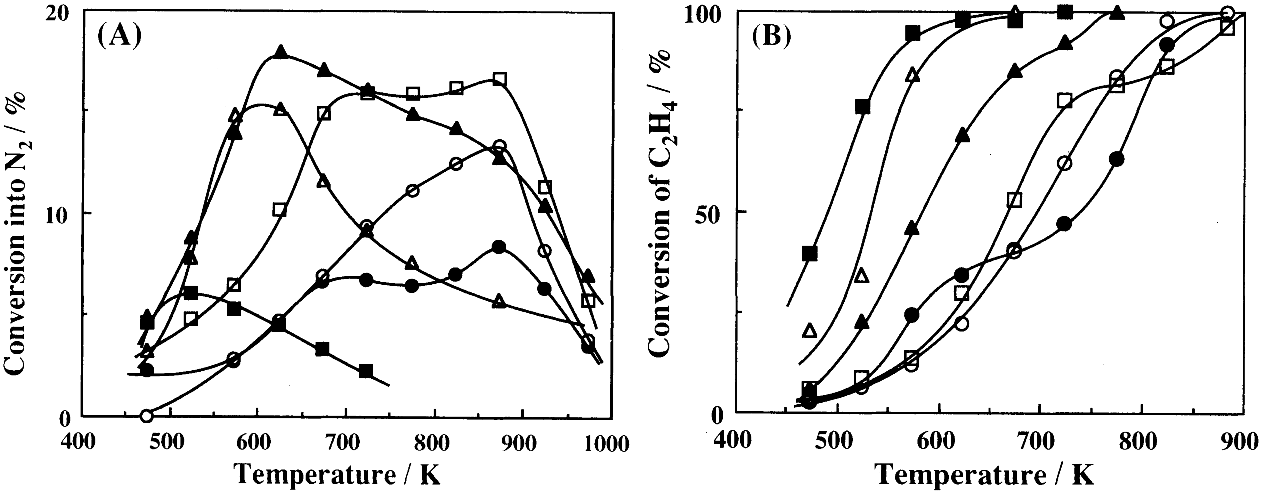

Fig. 1. Temperature dependence of the conversions into N_2 (A) and of C_2H_4 (B) on Cu/SiO_2-Al_2O_3 catalysts. The amount of copper loaded; ●, 0; ○, 1.3; □, 3.3; ▲, 3.7; △, 5.7; ■,13.0 wt%.

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