Enhancing and Inhibiting Effects of SO_2 on Selective Catalytic Reduction of NO_x by Ethene over Copper-Loaded Alumina Catalysts

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In both the selective catalytic reduction of NO by ethene and the similar reaction system except use NO_2 instead of NO, almost the same NO_x conversions to N_2 were obtained over Cu/Al_2O_3. In the presence of SO_2 in the feeds, however, the two NO_x reductions gave different results; the reduction of NO_2 was enhanced, while that of NO was inhibited.

The selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen (SCR-NO) has been investigated over various catalysts such as zeolites, metal oxides, and noble metals.[1] One of the most extensively studied metal oxides is alumina and it is often used as a metal-loaded alumina (M/Al_2O_3).[2] In SCR-NO, the role of NO_2 as an intermediate has been frequently reported,[3, 4] and in this connection SCR-NO_2 (a reaction system similar to SCR-NO except use NO_2 instead of NO) has been studied to understand the reaction pathway of SCR-NO. In SCR-NO_x over Al_2O_3 and M/Al_2O_3 (M: Co or Fe),[5] the reactivity of NO was different from that of NO_2, while over Pt/Al_2O_3[3] the reactivity of NO was the same as that of NO_2 in a wide range of reaction temperature.

It is well known that SO_2 in real exhaust gases inhibits most SCR-NO catalysts. However, the influence of SO_2 on SCR-NO has not been studied extensively.[6-11] During SCR-NO in the presence of SO_2 in the feed (SCR-NO-SO_2), SO_2 will influence the behavior of NO_2 as an intermediate. In that case, SCR-NO_2 in the presence of SO_2 (SCR-NO_2-SO_2) could be a model reaction. However, no study has been made on SCR-NO_2-SO_2. This communication describes the similarity of reactivity of NO and NO_2 in and the promoting or inhibiting effect of SO_2 on SCR-NOx over Cu/Al_2O_3.

Alumina used was γ-Al_2O_3 (143 $m^2 \cdot g^{-1}$ after calcination at 800 °C), which was prepared by hydrolyzing aluminum isopropoxide at 25 °C with stirring. A Cu/Al_2O_3 was prepared by a normal impregnation method using a solution of cupric acetate. After drying at 120 °C, the catalyst precursor was calcined at 500 or 800 °C for 4 h in air. Catalytic reactions were carried out with a fixed bed flow reactor by passing a reactant gas mixture at a total flow rate of 130 $ml \cdot min^{-1}$ over a catalyst (0.40 g). The gas mixture contained 1000 ppm NO_x, 2.0% O_2, 500 ppm C_2H_4, and 0-100 ppm SO_2 diluted in helium.

Figure 1 shows the results of SCR-NO and SCR-NO_2 over 1.0 wt% Cu/Al_2O_3 calcined at 500 °C. Interestingly, the activity for the SCR-NO was almost the same as that for the SCR-NO_2 in the whole temperature region. This suggests that NO and NO_2 are identical in the SCR-NO_x under the experimental conditions. Such a catalytic characteristic resembles that of Pt/Al_2O_3.[3] The conversions of ethene to CO_x (CO and CO_2) in the SCR-NO and SCR-NO_2 were approximately the same (Figure 1b). There was no formation of CO in both reactions.

In the SCR-NO-SO_2 (100 ppm), the maximum value of NO conversion (C_M) fell to about half a level of that for the SCR-NO (Figure 1a). In this reaction system SO_2 acted as a catalyst poison, although SO_2 has been reported to enhance SCR-NO over Pt/B_2O_3-SiO_2-Al_2O_3[8] and Co-ZSM-5.[10]

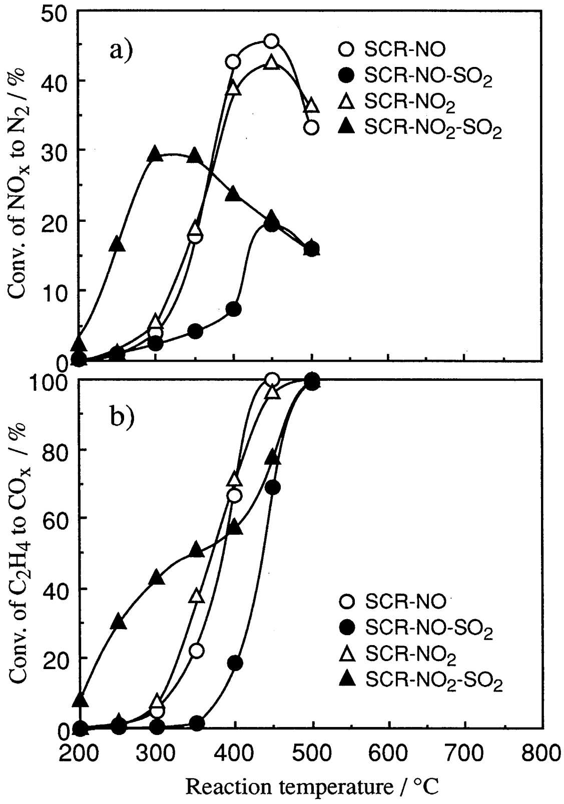

Figure 1. Temperature dependence of the catalytic activities of Cu(1.0 wt%)/Al_2O_3 catalyst calcined at 500 °C. Conditions: NO or NO_2 = 1000 ppm, C_2H_4 = 500 ppm, O_2 = 2.0%, SO_2 = 0 or 100 ppm, catalyst = 0.40 g, total flow rate = 130 $ml \cdot min^{-1}$, W/F = 0.18 $g \cdot s \cdot cm^{-3}$.

In the SCR-NO_2-SO_2, surprisingly, the activity was evidently higher than that for the SCR-NO_2 below *ca.* 350 °C. In other words, the temperature window (active temperature region) shifted to a lower temperature side. This result means that SO_2 acted as a promoting reagent in the SCR-NO_2-SO_2, and this effect, we think, is a new finding. During the SCR-NO_2-SO_2, there was a pretty complicated change in ethene oxidation activity with temperature; below 350 °C the oxidation activity was higher than that in the SCR-NO_2, while above the temperature, the order became reversed. In the SCR-NO_2-SO_2, formed much CO which was not observed in the SCR-NO_2 at all. The increment of CO_x below 350 °C consisted of a *ca.* equimolar mixture of CO and CO_2 and the decrement of CO_x above 350 °C was accompanied by increasing CO. It should be noted that the oxidation activity in the SCR-NO_2-SO_2 was higher than that in the SCR-NO-SO_2 below

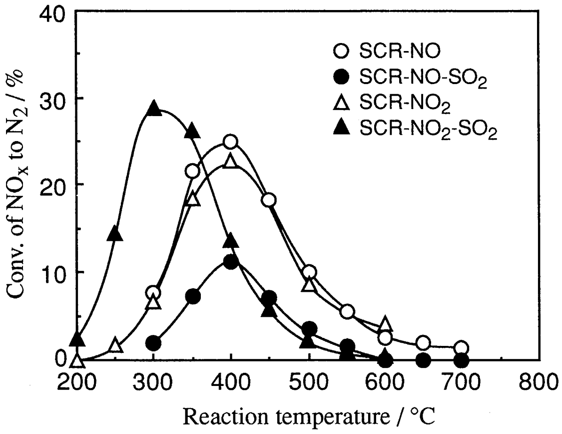

Figure 2. Temperature dependence of the catalytic activities of Cu(5.0 wt%)/Al_2O_3 catalyst calcined at 800 °C. Conditions: NO or NO_2 = 1000 ppm, C_2H_4 = 500 ppm, O_2 = 2.0%, SO_2 = 0 or 100 ppm, catalyst = 0.40 g, total flow rate = 130 ml·min^{-1}, W/F = 0.18 g·s·cm^{-3}.

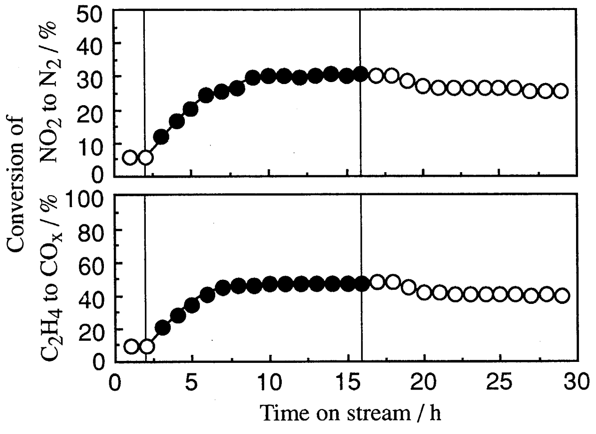

Figure 3. Catalytic activities of 1.0 wt% Cu/Al_2O_3 calcined at 500 °C for SCR-NO_2 (○) and SCR-NO_2-SO_2 (●) at 300 °C. Conditions: NO_2 = 1000 ppm, C_2H_4 = 500 ppm, O_2 = 2.0%, SO_2 = 0 or 100 ppm, catalyst = 0.40 g, total flow rate = 130 ml·min^{-1}, W/F = 0.18 g·s·cm^{-3}.

450 °C.

In SCR-NO_2-SO_2 (100 ppm) over 1.0 wt% Cu/Al_2O_3 calcined at 800 °C, the activity for SCR-NO_2 was again enhanced by SO_2 (not shown). Figure 2 shows the result of SCR-NO_2 over 5.0 wt% Cu/Al_2O_3 calcined at 800 °C, and also the result[12] of SCR-NO for comparison. The activity for the SCR-NO_2 was again similar to that of the SCR-NO. No CO was observed in both reactions. In this figure, the results of SCR-NO-SO_2 (100 ppm) and SCR-NO_2-SO_2 (100 ppm) over 5.0 wt% Cu/Al_2O_3 calcined at 800 °C were also shown. In the SCR-NO-SO_2, the C_M was reduced almost by half compared to that for the SCR-NO, although the temperature window did not shift. On the other hand, the temperature window for the SCR-NO_2-SO_2 shifted to a lower temperature side than that for the SCR-NO_2, and the C_M for the former was similar to that for the latter. The results of SCR-NO_2-SO_2 over the three Cu/Al_2O_3 catalysts mean that SO_2 acted as a promoting reagent for SCR-NO_2 over Cu/Al_2O_3 regardless of the Cu loading and calcination temperature.

To obtain information about the activity suppressing or promoting effect of SO_2 in SCR-NO_x-SO_2 over Cu/Al_2O_3, the activities for SCR-NO_x-SO_2 were investigated as a function of time on stream. In SCR-NO-SO_2 the activity decreased gradually to a steady value and simultaneously accumulation of sulfate ions proceeded gradually (not shown), like in the case of NO-CH_3OH-O_2-H_2O-SO_2 (10-500 ppm) reaction over Al_2O_3.[9] Figure 3 summarizes the results of a series of reactions, SCR-NO_2 → SCR-NO_2-SO_2 → SCR-NO_2 over 1.0 wt% Cu/Al_2O_3 calcined at 500 °C; all the reactions were carried out at 300 °C, which corresponds to the maximum-activity temperature for the SCR-NO_2-SO_2 (Figure 1b). The activity for SCR-NO_2 was only 5% in the first stage, but on introduction of SO_2 it increased gradually up to 30%, and on elimination of SO_2 it decreased very gradually, keeping the activity level higher than the original one (5%). After the series of reactions, sulfate ions were observed on the spent catalyst (not shown). The fact that the activity in the third stage was still higher than that in the first stage suggests that gaseous SO_2 is hardly responsible for the activity enhancement in the second stage but indirectly contributs to it through the surface sulfate ions. The gradual increase in activity in the second stage could be due to gradual accumulation of sulfate ions.

The findings that over Cu/Al_2O_3 NO and NO_2 behave similarly in SCR-NO_x and that SO_2 enhances SCR-NO_2 will greatly help for understanding the reaction pathway of SCR-NO and for developing a new SO_2-resistive SCR-NO catalyst system, respectively.

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