Enhancing Effect of SO_2 on Selective Catalytic Reduction of NO by Methanol over Ag/Al_2O_3

Tianle Zhu, Jiming Hao,* and Weibin Li
Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, P.R. China

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The effect of SO_2 on activity for NO reduction by methanol over Ag/Al_2O_3 in the presence of excess oxygen has been investigated. Selective catalytic reduction activity was not decreased but increased and most effective NO reduction temperature shifted from 200-250 °C to 300-350 °C by pre-sulfated Ag/Al_2O_3 or addition of SO_2 to reaction mixture.

The selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen has been investigated over catalysts such as zeolites, metal oxides, and noble metals.[1] Among various metal oxide-based catalysts, metal-supported alumina has been studied most intensively because of its high activity and stability. Miyadera et al.[2,3] firstly reported that Ag/Al_2O_3 catalysts were quite effective in reducing NO with propene and oxygen-containing organic compounds such as ethanol and acetone. However, water vapor and SO_2 have adverse effect on the reduction of NO with these reductants over Ag/Al_2O_3. And Ag/Al_2O_3 showed very little activity for NO reduction in the presence of water and excess oxygen when methanol was used as reductant.[3] These results have also been verified by authors in the preliminary experiments. On the other hand, we note that the effect of SO_2 on NO reduction by methanol over Ag/Al_2O_3 catalyst has seldom been studied although it has been investigated when propene, ethanol and fuel were used as reductants up to now.[4-6] In the paper, the authors report the enhancing effect of SO_2 on selective catalytic reduction of NO by methanol over Ag/Al_2O_3 catalysts.

Ag/Al_2O_3 catalysts were prepared in the same manner as described in Takagi's paper[7] unless the mole ratio of "nitric acid/AIP" was 0.2, the solvents were eliminated by heating them under atmosphere pressure and calcination time at 600 °C was 8 h. The silver loadings for Ag/Al_2O_3 catalysts prepared by single-step sol-gel method and impregnation method were 5% and 2% by weight and they were denoted as Ag/Al_2O_3 (Alk) and Ag/Al_2O_3 (Imp), respectively.

The catalytic activities of Ag/Al_2O_3 catalysts for NO reduction were evaluated using a fixed-bed flow reactor. A gas mixture containing 1100 ppm NO, 2000 ppm CH_3OH, 5% O_2, 0 or 10% H_2O and 0 or 80 ppm SO_2 in N_2 was fed to 0.5g of a catalyst at a rate of 350 $cm^3 \cdot min^{-1}$ unless otherwise stated. Methanol and H_2O were introduced into the system via two temperature-controlled bubble towers, respectively. A condenser removed water vapor in the post-catalyst stream. The catalyst temperature was monitored with a quartz-tube-covered thermocouple contacting with the inlet part of the catalyst bed and was raised stepwise with about 0.5 h at each temperature. NOx and methanol were analyzed by a chemiluminescent NO-NOx analyzer (Thermo Electron model 44) and an automotive emission gas analyzer (Horiba MEXA-554J series), respectively. The catalytic activity was expressed by the NOx conversion and methanol conversion.

Figure 1 shows the catalytic activities of Ag/Al_2O_3 (Alk) for selective catalytic reduction of NO with methanol in four kinds of reaction mixtures, i.e., without H_2O and SO_2, with 10% H_2O, with 80 ppm SO_2, and with 10% H_2O and 80 ppm SO_2. It is seen that the addition of 10% H_2O caused a significant loss of activity. On the other hand, it is quite surprising that the maximum NOx conversion over Ag/Al_2O_3 (Alk) was not decreased but increased and the most effective NO reduction temperature shifted from 200-250 °C to 300-350 °C by simultaneous addition of 10% H_2O and 80 ppm SO_2 or only addition of 80 ppm SO_2 to reaction mixture. This result means that SO_2 acted as a promoting reagent in the selective catalytic reduction of NO by methanol in the presence of excess oxygen, and this effect, we think, is a new finding. In addition, the methanol conversion curves shifted to higher temperature, as shown in Figure 1. And the presence of SO_2 led to an increase in methanol selectivity for NOx reduction (defined as NOx reduction/consumed methanol) in the temperature range of 150-400 °C corresponding to relatively high NOx reduction activity, which can be obtained by dividing the product of inlet NOx concentration and NOx conversion efficiency by that of inlet methanol concentration and methanol conversion efficiency. This suggests that SO_2 suppressed the undesirable methanol oxidation where methanol did not contribute to NOx reduction.

To further obtain information about the effect of co-existing SO_2 on the activity, the activities of NO reduction by methanol over Ag/Al_2O_3 (Alk) catalyst at 250 °C and 350 °C,

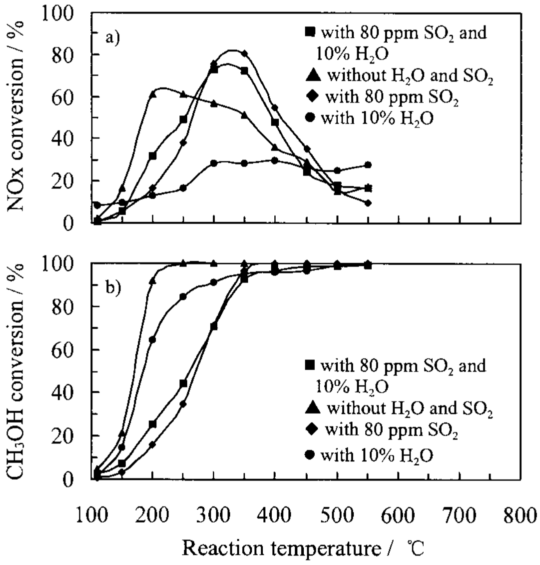

Figure 1. Temperature dependence of the catalytic activities of Ag/Al_2O_3 (Alk). Conditions: NO=1100 ppm, CH_3OH= 2000 ppm, O_2=5%, SO_2=0 or 80 ppm, H_2O=0 or 10%, W/F=0.0857 $g \cdot s \cdot cm^{-3}$.

which correspond to the maximum activity temperatures for NO reduction by methanol in the absence of SO_2 and water vapor and in the presence of SO_2, respectively, were investigated as a function of time, which are shown in Figure 2. The NO conversion at 350 °C was initially 51% without SO_2, but on introduction of SO_2 it increased gradually up to 80% and the activity basically remained unchanged after elimination of SO_2. The result was similar to that reported by Okazaki et al.[8] It is noted, however, that the latter was based on the reduction of NO_2 by ethene over 1.0 wt% Cu/Al_2O_3. On the other hand, the activity at 250 °C decreased gradually to a steady value by the addition of SO_2, like in the case of NO reduction by methanol over Al_2O_3.[9] As described in the Okazaki and Tabata's papers,[8,9] the activity suppressing or promoting effect of SO_2 on NO reduction by methanol over Ag/Al_2O_3 (Alk) catalyst can be attributed to the accumulation of sulfate ions on the catalyst surface. And it could be deduced the species containing sulfate ions is active for NO reduction by methanol. Its maximum activity temperature, however, is higher than that corresponding to sulfate ions-free Ag/Al_2O_3 (Alk) catalyst (Figure 1).

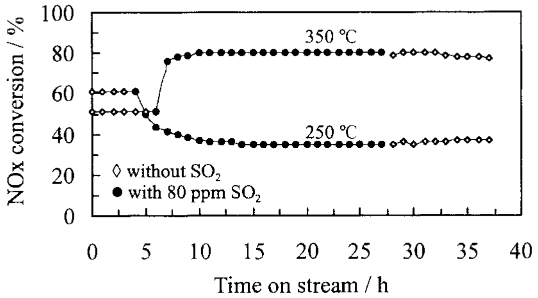

Figure 2. Effect of SO_2 on the time course of NOx conversion by methanol over Ag/Al_2O_3 (Alk) at 250 °C and 350 °C. Conditions: NO=1100 ppm, CH_3OH=2000 ppm, O_2=5% and SO_2=0 or 80 ppm, W/F=0.0857 g·s·cm^{-3}.

We also investigated the temperature dependence of the catalytic activities of Ag/Al_2O_3 (Alk) catalyst, pre-treated at 400 °C for 24 h in a flowing gas containing 500 ppm SO_2 diluted in air, for NO reduction by methanol in the presence of water and excess oxygen. The results are depicted in Figure 3. It is seen that the effect of co-existing SO_2 on NOx conversion and methanol conversion over the pre-sulfated catalysts was not obvious. And the presence of 10% H_2O did not decrease the activity while it decreased the activity of NO reduction by methanol over the un-sulfated Ag/Al_2O_3 (Alk) catalysts as shown in Figure 1, which suggests that the pre-sulfated Ag/Al_2O_3 (Alk) catalyst has excellent water-resistance. It is also seen that the NOx conversion and methanol conversion, compared with Figure 1, are similar to the ones corresponding to NO reduction by methanol over un-sulfated Ag/Al_2O_3 (Alk) in the presence of SO_2, which means that the pre-sulfated treatment can play same role as the addition of SO_2 to the reaction mixture. From a practical point of view, it is important that the pre-sulfated Ag/Al_2O_3 (Alk) catalysts have high activity in the presence of water vapor whether the SO_2 exists or not for sulfur content in fuel will gradually reduce and some lean burn emissions even do not contain SO_2 when alternative fuel is used.

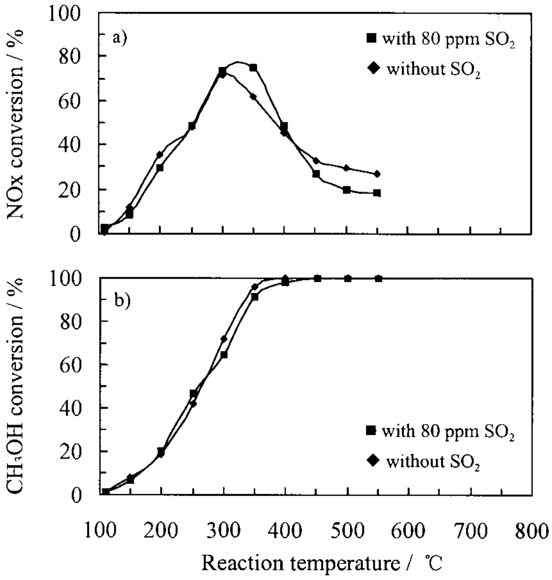

Figure 3. Temperature dependence of the catalytic activities of Ag/Al_2O_3 (Alk), pre-treated at 400 °C for 24 h in a flowing gas containing 500 ppm SO_2 diluted in air. Conditions: NO=1100 ppm, CH_3OH=2000 ppm, O_2=5%, H_2O=10%, SO_2=0 or 80 ppm, W/F=0.0857 g·s·cm^{-3}.

In addition, the activity of Ag/Al_2O_3 (Imp) catalyst prepared by impregnation method for NO reduction with methanol was also studied in this work. The results obtained were similar to that of Ag/Al_2O_3 (Alk) catalyst prepared by single-step sol-gel method.

In conclusion, it is confirmed that the activity of NO reduction by methanol over Ag/Al_2O_3 is enhanced and the maximum activity temperature shifts to higher temperature upon exposure to SO_2. This is attributed to the formation of sulfate species, which are active for NO reduction by methanol.

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