Selective catalytic reduction of NO with methane or ethanol over silver-alumina catalysts in the presence of high concentrations of SO_2 and H_2O

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SCR of NO with hydrocarbons has been under development for more than two decades as a promising technology for NO_x abatement. Ever since Ag/Al_2O_3 was reported as an active SCR catalyst [1], extensive work has been performed on elucidating the active structure, reaction mechanism, and the reported resistance of this catalyst to SO_2/H_2O [2,3].

In regard to the active sites on Ag-alumina for NO-SCR, literature reports [3,4] have pointed to the oxidized silver species as the catalytic sites for NO_x-SCR and to nanoparticles of silver as the catalytic sites for HC-combustion. In recent work in our lab, a nitric acid leaching method was applied to remove the silver particles from Ag-alumina prepared by co-gelation [5] in order to examine the activity and stability of the resulting silver aluminate surface. Silver cations were found in the Ag-alumina catalysts by UV-VIS (DRS). NO-O_2-TPD shows adsorption of NO_x on both alumina sites and nano-silver particles. However, the kinetics of the SCR reaction are similar for the leached and parent catalyst and the same apparent activation energies were found. Temperature programmed surface reaction experiments showed that the reaction light-off temperature (~300^{o}C), was higher than that of NO_x desorption from the silver nanoparticles. Hence, we conclude that only the NO_x species adsorbed on alumina participate in the SCR reaction. The SCR activity increases with the amount of oxidized alumina-bound silver. A reaction scheme involving alumina and Ag^+-O-Al sites is proposed. Silver nanoparticles are spectator species for the CH_4-SCR of NO.

On the other hand, silver particles are shown to be essential and even to promote the CH_4-SCR of NO in high concentrations of SO_2 (0.1%) in the gas stream [5]. Fig.1 shows the effect of SO_2 during CH_4-SCR over AlAg (11,CG) at 625^{o}C. At this temperature, addition of ~300ppm SO_2 enhances the NO conversion to N_2 to ~50%, while it decreases methane conversion from 55% to 25%. When the amount of SO_2 was increased to 1000ppm level, NO conversion stayed at ~40%. When SO_2 was removed from the stream, the NO conversion decreased with time and CH_4 conversion gradually increased. However, at 575^{o}C, a strong inhibition of SO_2 on both the NO and CH_4 conversion was observed, which could be due to competitive adsorption of SO_2 and the reactants at this temperature. The presence of SO_2 inhibited both the NO and CH_4 conversions over blank Al_2O_3 (CG) and one leached Ag-alumina catalysts at all temperatures, including 625^{o}C. The above phenomena will be discussed in terms of SO_2 adsorption and reaction on this type catalysts.

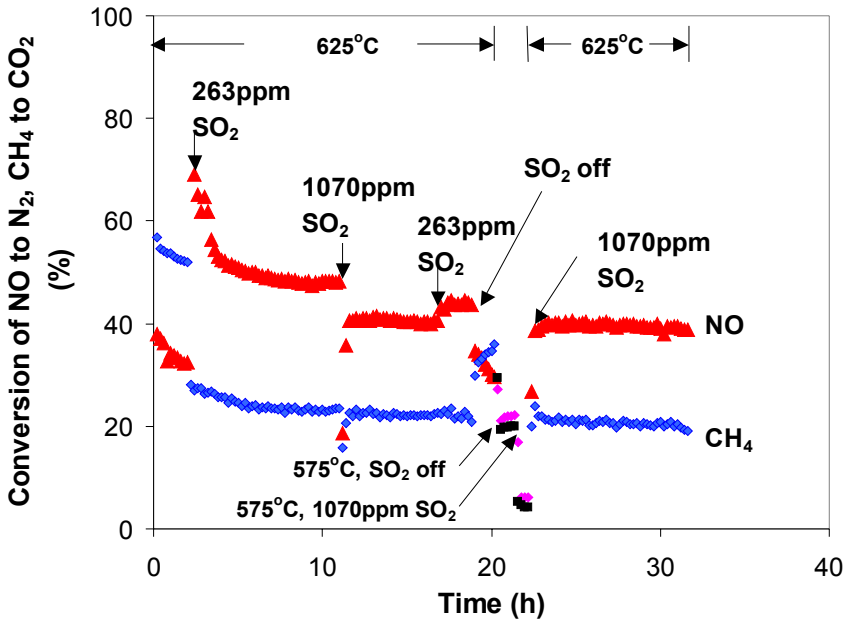

Fig. 1 Effect of SO_2 and H_2O on AlAg(11,CG) during CH_4-SCR of NO at 625°C. Feed gas: 0.25%NO-2%CH4-5%O2-0/0.1%SO2; S.V.=50,000h-1.

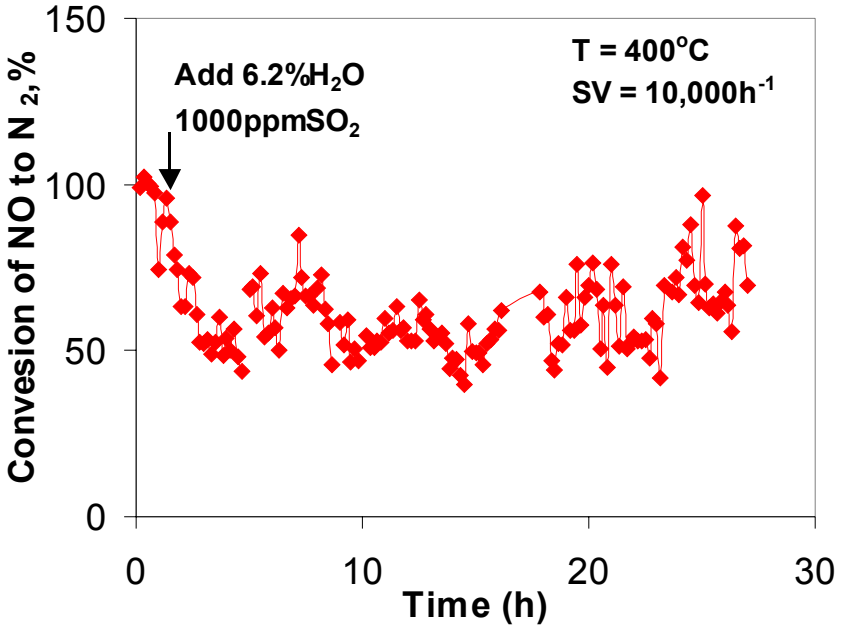

Fig. 2 Effect of SO_2 and H_2O on AlAg(3.8,CG) during ethanol-SCR of NO at 400°C. Feed gas: 300ppm NO-3600ppm ethanol-3%O2-0/6.2% H2O-0/1000ppm SO2.

Ethanol was examined in this work as an alternative NO_x reductant to methane, with the aim to lower the SCR reaction temperature. Fig. 2 shows the long-term activity and stability of AlAg(3.8,CG) during ethanol-SCR in the presence of SO_2 and H_2O at 400^oC. Addition of SO_2 and H_2O causes an initial drop of NO conversion from 100% to ~50%, however, after thorough aging (25h) in the SO_2-containing stream, the conversion rises to ~80%, which could indicate that sulfates had a promoting catalytic effect on the reaction as shown in Fig. 2. SO_2-TPD results over the aged catalysts will be presented. The role of silver nanoparticles in the SCR reaction in the presence of high amounts of SO_2 and H_2O will be compared to the silver particle-free catalysts.

References

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