Ga_2O_3/Al_2O_3 Prepared by Sol-Gel Method as a Highly Active Metal Oxide-Based Catalyst for NO Reduction by Propene in the Presence of Oxygen, H_2O and SO_2

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Ga_2O_3/Al_2O_3 prepared by sol-gel method showed excellent activity for the selective reduction of NO with propene in the presence of H_2O, compared with Al_2O_3, Ga_2O_3 and impregnated Ga_2O_3/Al_2O_3. Its high activity was hardly influenced by the presence of SO_2. It was suggested from the results of XPS studies that the presence of gallium oxide interacting strongly with alumina is responsible for the catalytic performance of Ga_2O_3/Al_2O_3.

The selective catalytic reduction of NO with hydrocarbons in the presence of oxygen is attracting great attention recently as a practical measure to remove NOx in diesel and lean burn engine exhausts. Although most of the reports have been related to zeolite-based catalysts,[1] we also found the activity of metal oxides for this reaction.[2] Among various metal oxide-based catalysts, metal-supported alumina has been studied most intensively because of its high activity and stability.[3] Miyadera and Yoshida[4] reported that Ga/Al_2O_3 was one of the highly active metal-supported alumina catalysts for NO reduction by propene. However, the activity was greatly decreased by coexisting H_2O. Recently, Shimizu et al.[5] investigated the catalytic performance of Ga_2O_3/Al_2O_3 prepared by impregnation method for the selective reduction of NO with methane and found that the activity increased with increasing gallium loading up to 33 wt%. In the present work, we studied the catalytic performance of Ga_2O_3/Al_2O_3 prepared by different methods and found that Ga_2O_3/Al_2O_3 prepared by sol-gel method showed quite high activity for NO reduction by propene in the presence of O_2, H_2O and SO_2.

Al_2O_3 was synthesized by hydrolysis of aluminium(III) tri-isopropoxide (AIP) in the same manner as described in a previous paper.[6] Ga_2O_3 was prepared from gallium hydroxide obtained by adding urea to an aqueous solution of gallium(III) nitrate and stirring at 90 °C for 10 h. Ga_2O_3/Al_2O_3 catalysts (abbreviated as Ga_2O_3/Al_2O_3(I) and (S)) were prepared by two different methods. Ga_2O_3/Al_2O_3(I) was prepared by impregnating above-mentioned alumina with an aqueous solution of gallium(III) nitrate. Ga_2O_3/Al_2O_3(S) was synthesized by sol-gel method using a mixed solution of AIP and gallium(III) nitrate dissolved in ethylene glycol. All the catalyst precursors were dried at 110 °C, followed by calcination at 600 °C for 5 h in flowing air. The gallium loading for Ga_2O_3/Al_2O_3(I) and(S) was fixed at 30 wt% as Ga_2O_3, unless otherwise stated. BET surface area was found to be as follows : Al_2O_3 200 m^2g^{-1}, Ga_2O_3 15 m^2g^{-1}, Ga_2O_3/Al_2O_3(I) 140 m^2g^{-1}, Ga_2O_3/Al_2O_3(S) 200 m^2g^{-1}.

The catalytic activity was measured by using a fixed bed flow reactor. A feed gas mixture containing 900 ppm NO, 860 ppm propene, 10% O_2, 9.1% H_2O and 0 or 100 ppm SO_2 diluted in helium was fed to 0.2 g of a catalyst at a rate of 66 cm^3min^{-1} (W/F=0.18 $gscm^{-3}$, SV=10000h^{-1}), unless otherwise specified. In the case of the experiments using the reaction gas mixture containing SO_2, the catalyst was pre-treated at 500 °C for 16 h in a flowing gas containing 300 ppm SO_2 diluted in air, in order to stabilize the catalyst. The effluent gas was analyzed by gas chromatography. The catalytic activity was expressed by the conversion of NO into N_2 and that of propene into COx ($CO+CO_2$). For catalyst characterization, XPS measurements were made in the regions of Ga_{2P} and Al_{2P}. The binding energy was corrected by the carbons contaminated. The peak area ratio (Ga_{2P}/Al_{2P}) was corrected by dividing the peak area, which was estimated through wave separation of XPS spectra, by the relative atomic sensitive factors.

Figure 1 shows the catalytic activity of Al_2O_3, Ga_2O_3/Al_2O_3(I), Ga_2O_3/Al_2O_3(S) and Ga_2O_3 for the selective reduction of NO with propene in the presence of H_2O. Ga_2O_3 showed very little activity for NO reduction. Al_2O_3 and Ga_2O_3/Al_2O_3(I) gave almost the same maximum NO conversion, although the effective temperature for NO reduction on the latter catalyst was lower than that on the former. Apparently, Ga_2O_3/Al_2O_3(S) showed excellent catalytic activity compared to Al_2O_3, Ga_2O_3/Al_2O_3(I) and Ga_2O_3. Since it is well known that sol-gel technique is capable of preparing catalysts with highly dispersed species,[6] the presence of gallium oxide interacting strongly with alumina would be related to the high activity of Ga_2O_3/Al_2O_3(S).

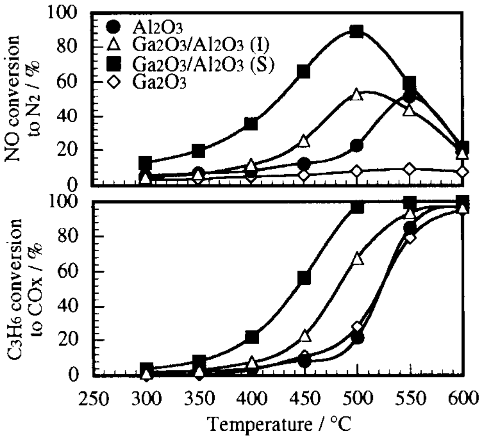

Figure 1. Catalytic activities of Al_2O_3, 30 wt% Ga_2O_3/Al_2O_3(I), 30 wt% Ga_2O_3/Al_2O_3(S) and Ga_2O_3 for NO reduction by propene in the presence of H_2O. Reaction conditions: NO=900 ppm, C_3H_6=860 ppm, O_2=10%, H_2O=9.1%, W/F=0.18 $gscm^{-3}$.

The catalytic activity for NO reduction by propene in the presence of H_2O and SO_2 was also measured for Al_2O_3, Ga_2O_3/Al_2O_3(I) and Ga_2O_3/Al_2O_3(S). As can be seen by comparing Figures 1 and 2, the activity of Al_2O_3 and Ga_2O_3/Al_2O_3(I) for NO reduction was depressed considerably by SO_2, whereas SO_2 inhibited slightly propene oxidation. On the other hand, it is quite surprising that NO conversion on Ga_2O_3/Al_2O_3(S) was not decreased but increased by SO_2 at temperatures below 450 °C. Since propene conversion to COx was also increased, the enhancement of NO reduction activity of Ga_2O_3/Al_2O_3(S) by SO_2 is not due to the inhibition of propene combustion by O_2 which decreases NO reduction selectivity. Probably SO_2 adsorption improves the catalytically active sites of Ga_2O_3/Al_2O_3(S) for NO reduction.

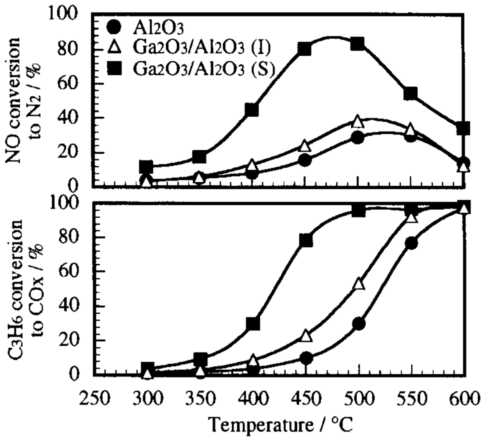

Figure 2. Catalytic activities of Al_2O_3, 30 wt% Ga_2O_3/Al_2O_3(I) and 30 wt% Ga_2O_3/Al_2O_3(S) for NO reduction by propene in the presence of H_2O and SO_2. Reaction conditions: NO=900 ppm, C_3H_6=860 ppm, O_2=10%, H_2O=9.1%, SO_2=100 ppm, W/F= 0.18 $gscm^{-3}$.

The results of XPS measurements were summarized in Table 1. The peak area ratio (Ga_{2p}/Al_{2p}) for Ga_2O_3/Al_2O_3(I) was higher than that for Ga_2O_3/Al_2O_3(S), suggesting that most of Ga_2O_3 was deposited on the surface of Ga_2O_3/Al_2O_3(I). The binding energy of Ga_{2p} for Ga_2O_3/Al_2O_3(S) was higher than that for Ga_2O_3/Al_2O_3(I). In addition, a difference in the Auger parameter of Ga species, which is the sum of the binding energy of Ga_{2p} and the Auger kinetic energy of $Ga_{(MNN)}$,[7] was observed between Ga_2O_3/Al_2O_3(I) and (S). Wagner et al.[7] measured the Auger parameter of Al species for several samples and revealed that it decreased with increasing tetrahedral Al ions. Ga_2O_3 is also known to have both tetrahedral and octahedral Ga ions.[8] Shimizu et al.[5] reported that low-coordinated Ga ions, i.e. tetrahedral Ga ions, is related to the high activity of Ga_2O_3/Al_2O_3 for NO reduction by methane. Consequently, it is suggested that the high catalytic performance of Ga_2O_3/Al_2O_3(S) is induced by a lot of tetrahedral Ga ions.

Table 1. Summary of peak area ratios, line energies and Auger parameters obtained for Ga_2O_3, 30 wt% Ga_2O_3/Al_2O_3(I) and 30 wt% Ga_2O_3/Al_2O_3(S)

Catalyst	Peak area ratio	Binding energy	Auger kinetic energy	Auger parameter[a]
	Ga_{2p}/Al_{2p}	Ga_{2p} / eV	$Ga_{(MNN)}$/ eV	/ eV
Ga_2O_3	-----	1118.10	1063.00	2181.10
Ga_2O_3/Al_2O_3 (I)	0.189	1118.37	1061.99	2180.36
Ga_2O_3/Al_2O_3 (S)	0.147	1118.53	1061.62	2180.15

[a] Auger parameters are the sum of the binding energy of Ga_{2p} and the Auger kinetic energy of Ga(MNN).[7]

It was found that the optimum loading of Ga_2O_3 for Ga_2O_3/Al_2O_3(S) was 50 wt%. Figure 3 shows the catalytic activity of 50 wt% Ga_2O_3/Al_2O_3(S) in the presence of H_2O and SO_2 at SV=40000h^{-1}. The maximum NO conversion was as high as 80% at 500 °C in the absence of SO_2. The addition of SO_2 into the reaction gas mixture caused a slight decrease of NO conversion. However, the maximum NO conversion of 65% was still attained at 500 °C. As described before, promotional effect of SO_2 was observed on 30 wt% Ga_2O_3/Al_2O_3(S) at SV=10000h^{-1}, while on 50 wt% Ga_2O_3/Al_2O_3(S) negative effect of SO_2 was recognized. Since it was confirmed in separate experiments that SO_2 enhanced NO reduction on 30 wt% Ga_2O_3/Al_2O_3(S) even at SV=40000h^{-1}, the effect of SO_2 would be dependent upon Ga_2O_3 content of the catalyst. The surface structure of the catalyst might be different depending on Ga_2O_3 content. The initial NO conversion on 50 wt% Ga_2O_3/Al_2O_3(S) was also restored by removing SO_2 from the reaction gas mixture. This means that the effect of SO_2 is not irreversible catalyst deterioration but reversible reaction inhibition.

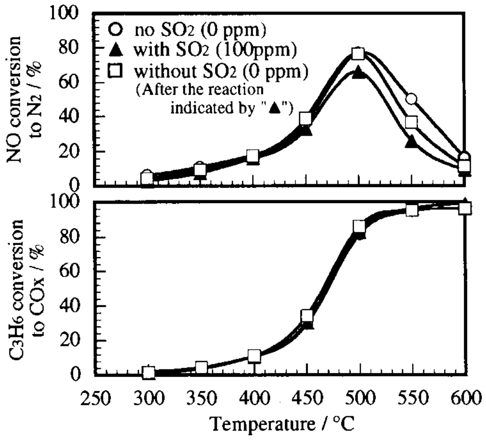

Figure 3. Catalytic activities of 50 wt% Ga_2O_3/Al_2O_3(S) for NO reduction by propene in the presence of H_2O and SO_2 at SV=40000 h^{-1}. Reaction conditions: NO=900 ppm, C_3H_6=860 ppm, O_2=10%, H_2O=9.1%,SO_2=0 or 100 ppm,W/F=0.05 $gscm^{-3}$.

In conclusion, it was confirmed that Ga_2O_3/Al_2O_3(S) prepared by sol-gel method showed excellent activity for the selective reduction of NO with propene in the presence of H_2O and SO_2. The presence of tetrahedral Ga ions is probably related to the catalytic performance of Ga_2O_3/Al_2O_3.

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