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Enhanced Catalytic Activity of Silica-Deposited Alumina for Selective Reduction of Nitrogen Monoxide by Ethene in Oxidizing Atmosphere

Noriyasu OKAZAKI, Takuya KOHNO, Ryo INOUE, Yuzo IMIZU,† and Akio TADA*
Department of Applied Chemistry, Kitami Institute of Technology, Kitami, Hokkaido 090
†Department of Materials Science, Kitami Institute of Technology, Kitami, Hokkaido 090

The effect of silica deposition by CVD method onto alumina catalyst on its catalytic activity for the titled reaction was examined. The deposition of a small amount of silica resulted in the enhancement of the activity, whereas the activity was greatly affected by the variation of alkoxy silane as a source of silica.

The selective reduction of nitrogen monoxide by hydrocarbons in an oxidizing atmosphere has been continuously received a great deal of attention.1-6) Among the active catalysts for the reaction, alumina would be a promising candidate for the practical catalyst and/or support, since alumina is one of the widely used, cheap, heat-stable materials.7) To improve the catalytic activity of alumina, substantial studies have been made on loading of transition metal elements;8, 9) however, there is few study concerning the additive effect of nontransition metals.10, 11) We recently reported that the deposition of silica submonolayer by CVD method improved the catalytic activities of alumina for several kinds of reactions including isomerization of olefins12) and exchange reaction of butene with D_2.13) In this study we have examined the effect of deposited silica on the catalytic activity of alumina as part of a program directed toward the development of the highly effective alumina-based catalysts for the titled reaction. We wish to report that a small amount of silica is effective in enhancing the catalytic activity and that this enhancement is greatly affected by the variation of alkoxy silane as a source of silica.

Silica was deposited on Al_2O_3 by chemical vapor deposition (CVD); alkoxy silanes such as $(CH_3)_xSi(OC_2H_5)_{4-x}$ (X=0, 2) and $Si(OCH_3)_4$ were adsorbed on a 773 K-pretreated Al_2O_3 (JRC-ALO4) followed by desorbing excess silane at temperatures from 298 K to 773 K to form submonolayer of covalently anchored silica precursor which was finally converted to silica by O_2 treatment at 773 K. Such a catalyst will be denoted as SiO_x/Al_2O_3 hereinafter. The amount of deposited silica was measured by using a quartz spring balance.

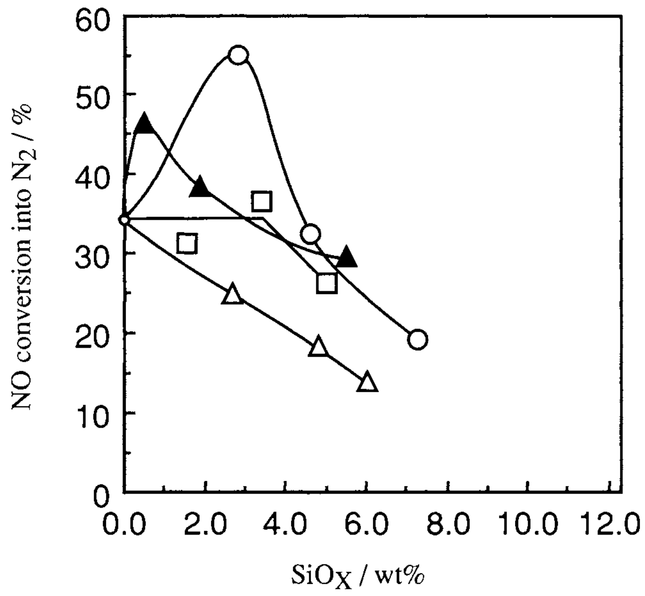

Fig. 1. Maximun activities of SiO_x/Al_2O_3 catalysts for NO conversion into N_2 as a functional of SiO_x weight. SiO_x/Al_2O_3 were prepared by CVD method using; ○, $(CH_3)_2Si(OC_2H_5)_2$; □, $Si(OC_2H_5)_4$; △, $Si(OCH_3)_4$; ▲, the catalyst was prepared by a different type of CVD method in which $Si(OCH_3)_4$ directly reacted on Al_2O_3 surface at 573 K followed by hydrolysis by water.
NO, 1000 ppm; O_2, 2%; C_2H_4, 500 ppm; catalyst weight, 0.4 g; total flow rate, 130 ml·min^{-1}.

Prior to the reaction the catalyst was pretreated at 1073 K under He stream for 4 h. The reaction was carried out with a fixed bed flow reactor. A mixture of 1000 ppm NO, 500 ppm C_2H_4, 2% O_2, and helium (balance) was fed onto a 0.4 g of a catalyst bed at a rate of 130 cm^3(STP)·min^{-1}. After a steady-state is reached, products were analyzed by gas chromatography. The catalytic activity was evaluated by the level of conversion into N_2 since it was confirmed that N_2O formation was negligible under the present conditions.

Figure 1 shows the maximum activities of SiO_x/Al_2O_3 catalysts for NO conversion into N_2 as a function of SiO_x weight. The maximum activity data were obtained from the reduction of NO as a function of reaction temperature as shown in Fig. 2. The most remarkable feature is the increase in the activity of alumina when silica was deposited by the CVD using $(CH_3)_2Si(OC_2H_5)_2$ (It should be noted that silica itself is inactive and conventional SiO_2-Al_2O_3 is less active than Al_2O_3[10]). Indeed, 2.8 wt% of silica increased the activity by a factor of 1.6, and further deposition caused a decrease in activity. In sharp contrast, silica deposited from $Si(OCH_3)_4$ were detrimental from the early stage of the deposition. In the case of $Si(OC_2H_5)_4$ used, the activity of alumina was not significantly affected at the range of loading examined in this study. Of particular interest is that the catalysts exhibited quite different activities in spite of the same amounts of silica deposited on alumina, indicating that silica acts as both a modifier and a site-blocking agent for NO reduction into N_2 on Al_2O_3.

The temperature dependence of the conversions of NO into N_2 and of C_2H_4 into CO_2 on SiO_x/Al_2O_3 are

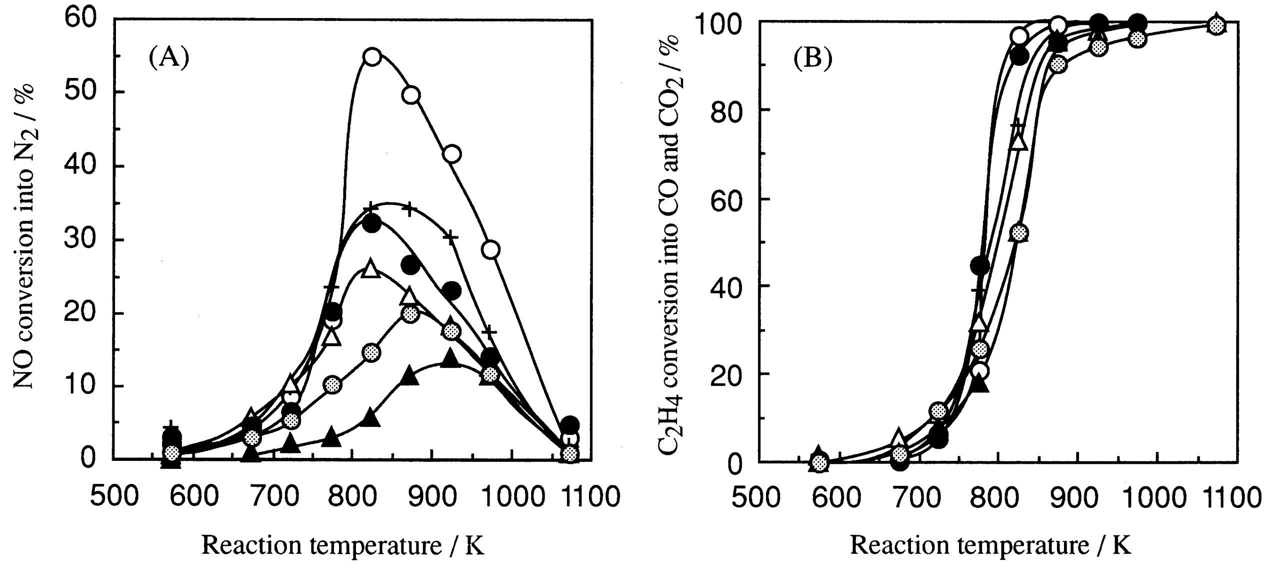

Fig. 2. Variation in NO conversion into N_2 (A) and C_2H_4 conversion into CO and CO_2 (B) on SiO_x/Al_2O_3 as a function of reaction temperature. SiO_x/Al_2O_3 were prepared by CVD method using;

○, $(CH_3)_2Si(OC_2H_5)_2$ (2.8 wt%); ●, $(CH_3)_2Si(OC_2H_5)_2$ (4.6 wt%); ◍, $(CH_3)_2Si(OC_2H_5)_2$ (7.3 wt%);
△, $Si(OC_2H_5)_4$ (5.0 wt%); ▲, $Si(OCH_3)_4$ (6.1 wt%); +, Al_2O_3 (JRC-ALO4).
NO, 1000 ppm; O_2, 2%; C_2H_4, 500 ppm; catalyst weight, 0.4 g; total flow rate, 130 ml·min^{-1}.

shown in Fig. 2 in comparison with that on Al_2O_3. Upon deposition of silica, the maximum activities of catalysts prepared from $(CH_3)_2Si(OC_2H_5)_2$ except for the catalyst containing 7.3 wt% of silica for NO conversion were attained at 823 K which is slightly lower than that observed on Al_2O_3, whereas the maximum activity of the catalyst prepared from $Si(OCH_3)_4$ was observed at higher than 873 K. Similarly, on the former catalysts the formation of CO and CO_2 from C_2H_4 readily occurred at lower temperature than on Al_2O_3. These results show that the capability of the SiO_x/Al_2O_3 prepared from $(CH_3)_2Si(OC_2H_5)_2$ for the oxidation of C_2H_4 by oxygen or NO was improved. The increase in the temperature at which the maximum activity of the catalyst prepared from $(CH_3)_2Si(OC_2H_5)_2$ (7.3 wt%) could be explained by the decrease in its activity due to excess silica deposition (cf. Fig. 1).

In order to examine to what extent the oxidation of C_2H_4 occurs with either NO or O_2, NO conversion levels are plotted against C_2H_4 conversion levels to CO and CO_2, as shown in Fig. 3. Clearly, among the all catalysts examined in this study the oxidation of C_2H_4 with NO more readily occurs on the SiO_x/Al_2O_3 prepared from $(CH_3)_2Si(OC_2H_5)_2$, indicating again that the silica deposited from $(CH_3)_2Si(OC_2H_5)_2$ is an excellent modifier to improve the activity of Al_2O_3 for the selective reduction of NO.

The structures of silica deposited from various kinds of silanes were not revealed in this study, since initially formed SiO_x submonolayer might structurally change during the pretreatment at 1073 K under He atmosphere. Despite of lack of structural information, similar enhancement of the activity was observed on SiO_x/Al_2O_3 by different type of CVD method using $Si(OCH_3)_4$ developed by M. Niwa.[14)] As shown in Fig. 1, when $Si(OCH_3)_4$ directly reacted on Al_2O_3 surface at 573 K followed by hydrolysis by water, the resulting SiO_x/Al_2O_3 exhibited the enhanced activity by a factor of 1.4. Therefore, the activity of silica-deposited Al_2O_3 for the selective reduction of NO is considered to depend on deposition conditions as well as kinds of silanes used.

We conclude from these results that the silica deposited by CVD method using $(CH_3)_2Si(OC_2H_5)_2$ and/or $Si(OCH_3)_4$ is an excellent modifier to improve the activity of Al_2O_3 for the selective reduction of NO by ethene in an oxidizing atmosphere.

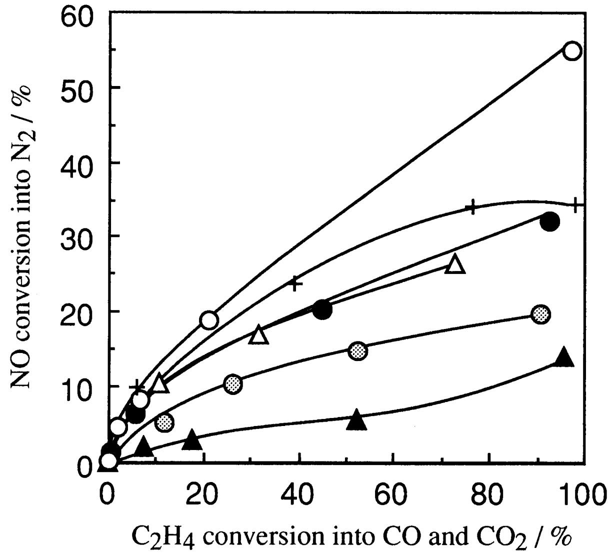

Fig. 3. NO conversion versus C_2H_4 conversion plots during the reduction of NO with C_2H_4 on SiO_x/Al_2O_3. SiO_x/Al_2O_3 were prepared by CVD method using; ○, $(CH_3)_2Si(OC_2H_5)_2$ (2.8 wt%); △, $Si(OC_2H_5)_4$ (5.0 wt%); ●, $(CH_3)_2Si(OC_2H_5)_2$ (4.6 wt%); ▲, $Si(OCH_3)_4$ (6.1 wt%); ◍, $(CH_3)_2Si(OC_2H_5)_2$ (7.3 wt%); +, Al_2O_3 (JRC-ALO4).

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