Selective catalytic reduction of NO by C_3H_6 over Co/Al_2O_3 catalyst with extremely low cobalt loading

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In order to reveal the optimum Co loading, the selective catalytic reduction of NO with C_3H_6 over Co/Al_2O_3 catalyst was studied in a systematic fashion by varying the amount of cobalt oxide. It was found that upon loading a small amount of cobalt oxide (namely 0.5 wt% on a Co metal basis), the combination between Co(II) acetate salt and a high-purity alumina provided an active catalyst in the presence of excess oxygen and water. TPR measurement showed the presence of Co species other than $CoAl_2O_4$ spinel in the most excellent performance catalyst, from which the active sites should be produced.

KEY WORDS: NO reduction; Co/Al_2O_3 catalyst; extremely low loading of Co; maximum Co loading of 0.5 wt%

1. Introduction

Developing a high performance catalyst for the selective catalytic reduction (SCR) of NO_x with hydrocarbons is an urgent matter, because the SCR catalyst system should open a possible route for the suppression of NO emission from the automotive lean-burn or diesel engine. Since the pioneering studies on Cu-ZSM-5 zeolite by Iwamoto *et al.* [1] and Held *et al.* [2], a variety of metal ion-exchanged zeolites have been studied extensively as an SCR catalyst [3]. Other than the zeolite-based catalyst system, Hamada *et al.* found that certain single metal oxides and supported metal oxides exhibited an appreciable capacity for the reduction of NO with propane or propene in the presence of excess oxygen [4,5]. A supported metal oxide catalyst is superior in hydrothermal stability to a zeolite-based catalyst. Therefore, a high performance de-NO_x system consisting of a metal oxide-based catalyst will be more promising for an automotive lean-burn engine.

Among supported metal oxides, alumina-supported cobalt oxide (denoted hereafter as Co/Al_2O_3) is a prominent catalyst, because such a catalyst was reported to be stable in the presence of SO_2 and water [6]. It was also reported that the activity of Co/Al_2O_3 catalyst was dependent upon both a cobalt precursor and a support material: a good catalyst was obtained by using cobalt acetate salt as the precursor and an alumina support [5]. There seems, however, to be a slight controversy in the optimal Co loading. Hamada *et al.* [7] reported that a small amount of Co loading resulted in a high performance in case of their impregnation catalyst. At a $W/F = 0.19\,g\,s\,cm^{-3}$, the NO conversion was 55% at 450 °C and 50% at 400 °C for Co loadings of 0.1 and 0.5 wt%, respectively. It was reported in their recent paper that the impregnation of alumina, prepared by a sol-gel method, with a cobalt acetate aqueous solution resulted in exhibiting a higher performance for the Co loading of 0.8–1.8 wt%: the highest NO conversion was 88–90% at the temperature of 350–400 °C [8]. However, the catalytic activity decreased considerably when water was present in the reactant gases. On the other hand, an optimum activity was observed at a higher Co loading in the case of a Co/Al_2O_3 catalyst prepared by a sol-gel method [6,9]. Therefore, the effect of Co loading on the SCR of NO with propene should be studied more systematically in order to optimize the Co loading for a better catalytic performance.

2. Experimental

The alumina used was a commercially obtainable θ-phase one (tradename of TM-100, Taimei Chemicals Co.), which was synthesized by thermally decomposing $Al(NH_4)CO_3(OH)_2$. The TM-100 alumina, originally developed for the synthesis of sinterable α-alumina ceramics, was characterized by its high purity (>99.99%) and very low bulk density ($0.16\,g\,cm^{-3}$). Before use, the alumina was heated at 1100 °C for 5 h (resultant specific surface area, $96\,m^2\,g^{-1}$). Supported cobalt oxide catalyst was prepared by impregnating the

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alumina with an aqueous solution of Co(II) acetate tetrahydrate (Wako Pure Chemical Industries Ltd.). The cobalt oxide content in the Co/Al$_2$O$_3$ catalyst was varied from 0.1 to 30 wt% on a cobalt metal basis by changing the concentration of Co(II) acetate in the starting aqueous solution.

XRD patterns were taken on an MXP3 powder diffractometer with Cu Kα radiation (MAC Science Inc.), which was operated at 40 kV and 20 mA. The UV–vis spectrum was measured by using a U-3000 UV–vis spectrophotometer (Hitachi Inc.). TPR experiments were carried out using H$_2$/Ar (H$_2$, 5%) under a flow rate of 30 ml min^{-1}. The amount of catalyst was 150 mg for the Co loading of 0.5 wt%, while a 50 mg sample was used for higher Co loadings. The temperature ramp was 10 °C min^{-1}.

Catalyst activity was measured with a fixed bed flow type apparatus with a U-shaped quartz glass reactor (i.d., 8 mm ∅). Prior to reaction, the catalyst (usually 0.3 g) was heated in flowing O$_2$ at 500 °C for 1 h. The feed gas consisted of a mixture of 750 ppm NO, 680 ppm C$_3$H$_6$, 4% O$_2$ and N$_2$ was a balance, unless otherwise described. The total gas flow rate was 165 ml min^{-1} and the space velocity corresponded to about 15 000 h^{-1}. The effects of O$_2$ and water were examined, respectively, by varying the O$_2$ concentration in the reactant gases from 4 to 19% and by saturating the balancing N$_2$ gas with H$_2$O (H$_2$O concentration, 20 vol%). The concentrations of NO and NO$_2$ were analyzed with a chemiluminescence method by using a CLA-510SS NO$_x$ analyzer (HORIBA Inc.) with a sampling rate of 100 ml min^{-1}. Other effluent gases were analyzed by a TCD gas chromatograph (Shimadzu GC-8A) equipped with Porapack Q and molecular sieve A as a separation column.

3. Results and discussion

3.1. Catalyst characterization

To characterize the catalyst, XRD, UV–vis spectroscopy, and TPR measurements were performed. The UV–vis spectroscopy of Co/Al$_2$O$_3$ catalysts with Co loading >2 wt% exhibited a clear distinct triplet centering at 540, 580 and 625 nm attributed to tetrahedral Co^{2+} ions in CoAl$_2$O$_4$ [6]. The triplet absorption was still discernible for 1 wt% Co/Al$_2$O$_3$, while it was absent for samples with Co loading <0.5 wt%.

Figure 1 shows the XRD patterns of Co/Al$_2$O$_3$ catalyst with different Co loadings. For Co loading <2 wt%, the XRD pattern is virtually the same as that of θ-phase alumina. For Co loading >3 wt%, the intensity of diffraction peaks attributable to Co$_3$O$_4$ or CoAl$_2$O$_4$ increases at the expense of that of θ-alumina. Although it is difficult to distinguish the diffraction peaks of Co$_3$O$_4$ from those of CoAl$_2$O$_4$, the decrease in the intensity of peaks corresponding to the original

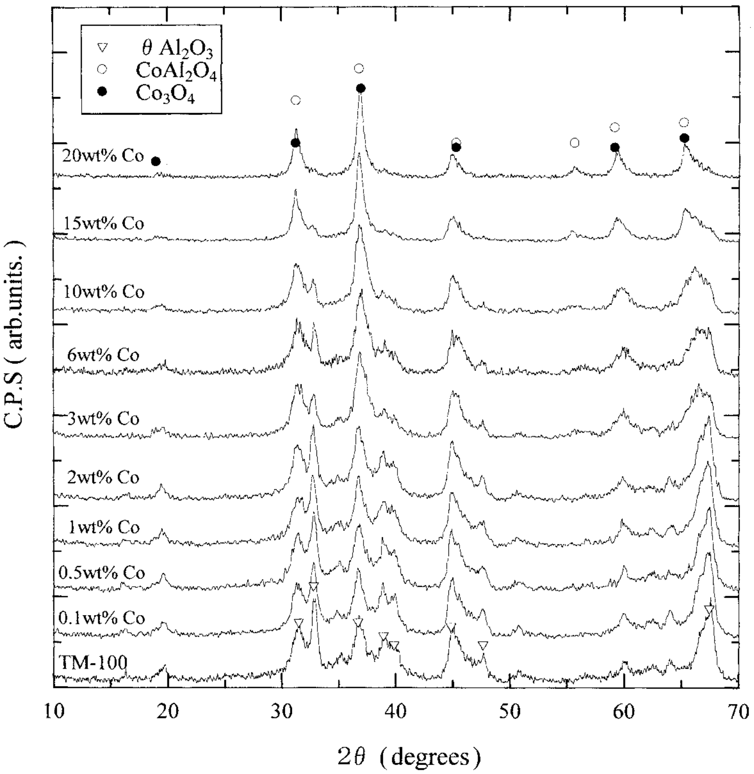

Figure 1. XRD patterns of Co/Al$_2$O$_3$ catalysts with various Co loadings. ▽: θ-Al$_2$O$_3$, ○: CoAl$_2$O$_4$, ●: Co$_3$O$_4$.

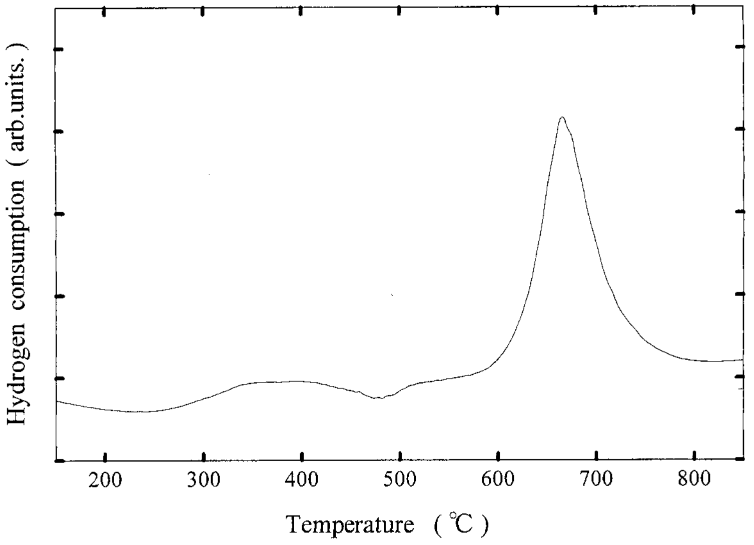

Figure 2. TPR profile of 0.5 wt% Co/Al$_2$O$_3$ catalyst. The flow rate of the H$_2$/Ar mixture gas (H$_2$, 5%) was 30 ml mn^{-1} and the temperature ramp was 10 °C min^{-1}.

θ-alumina leads us to conclude that CoAl$_2$O$_4$ spinel is the major phase generated.

The TPR profile for 0.5 wt% Co/Al$_2$O$_3$ catalyst shown in figure 2 exhibits a doublet, one at 400 °C and the other around 700 °C. Since CoAl$_2$O$_4$ spinel is generally difficult to reduce, the peak at around 700 °C has been ascribed to the reduction of CoAl$_2$O$_4$, although the peak temperature is slightly less than that reported in the literature [10]. The peak appearing at 400 °C has been attributed to the reduction of cobalt oxide (Co$_3$O$_4$ or CoO). The observed broad peak for the reduction of cobalt oxide might result from its highly dispersed state on the alumina surface to interact strongly with each other. However, there is no XRD distinct evidence for the presence of bulk Co$_3$O$_4$ or CoO in the sample.

3.2. Catalyst activity

Figure 3 shows the conversion of NO to N$_2$ as a function of the reaction temperature. While the catalytic activity of the TM-100 alumina is very low, the addition of cobalt oxide increases the NO conversion. With the elevation of the reaction temperature, NO conversion increases to reach a maximum value and then decreases. This relationship between NO conversion and the reaction temperature has been observed in the literature and the oxidation of propene to CO$_2$ and H$_2$O, preferably occurring at higher temperatures, should be responsible for the decrease in NO conversion above 450 °C. It is interesting to note in figure 3 that the addition of a small amount of cobalt oxide brings about a better performance. Indeed,

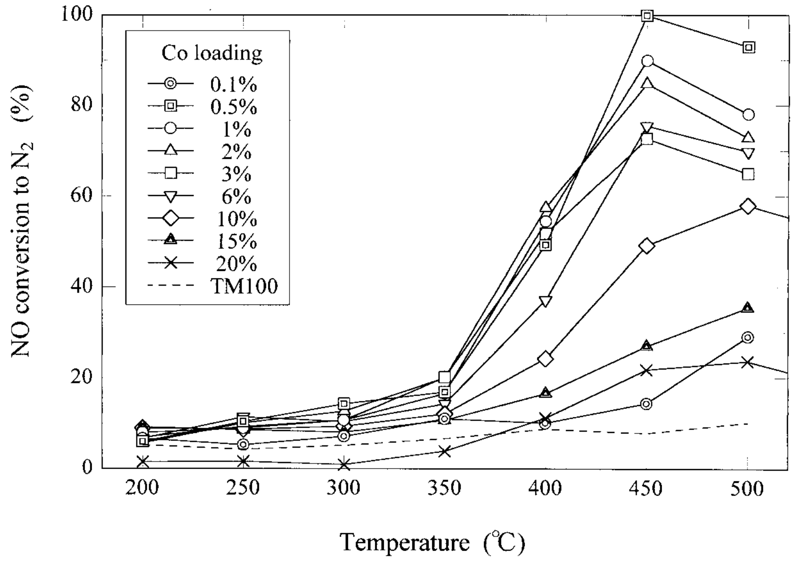

Figure 3. NO conversion to N$_2$ as a function of the reaction temperature. Catalyst weight: 0.3 g, the feed gas: 750 ppm NO, 680 ppm C$_3$H$_6$, and 4% O$_2$ (N$_2$ was a balance), total gas flow rate: 165 ml min^{-1} (the space velocity corresponds to about 15 000 h^{-1}.)

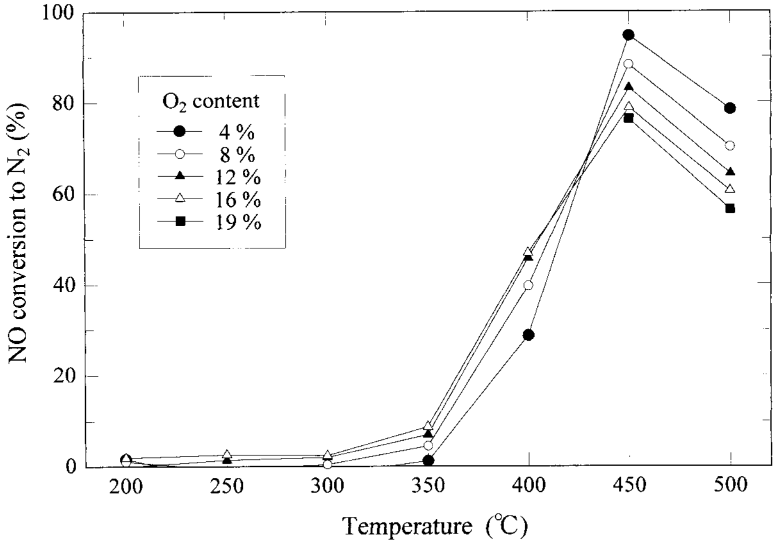

Figure 4. Effect of O$_2$ concentration on NO reduction to N$_2$ over 0.5 wt% Co/Al$_2$O$_3$ catalyst. Except for the O$_2$ concentration, the other conditions are the same as those described in figure 3.

NO reduction is close to 100% on 0.5 wt% Co/Al$_2$O$_3$ at 450 °C. The activities of 1 and 2 wt% Co/Al$_2$O$_3$ are still high, and the NO conversions achieved at 450 °C are 90 and 85%, respectively. However, further increase in Co loading decreases the NO conversion. It is possible that the oxidation of propene is being promoted by the excess amount of cobalt oxide, and as a consequence the NO conversion declines. It should also be noted that the catalyst with too small an amount of cobalt oxide, namely 0.1 wt%, does not exhibit an appreciable NO conversion. Thus in the combination between Co(II) acetate salt and TM-100 alumina, 0.5 wt% has been found to be an optimum Co loading for selective NO reduction with propene in the presence of oxygen.

It is known that the catalyst performance is affected by both O$_2$ and water present in the reactant gases. Figures 4 and 5 show the effects of the O$_2$ concentration and H$_2$O on selective NO reduction with propene over the best catalyst of the present study. Figure 4 shows that a maximum NO conversion can be attained at the reaction temperature of 450 °C for all the O$_2$ concentrations examined and a conversion of above 75% can be achieved even at an O$_2$ concentration of 19%, although the effect observed is different between high and low reaction temperature ranges. With increasing O$_2$ concentration, NO conversion gradually decreases at a temperature >450 °C, while it increases at a temperature <450 °C. In figure 5, it can be noticed that a 20 vol% vapor shifts the temperatures, for the maximum NO conversion, to a higher one. However, the 0.5 wt% Co/Al$_2$O$_3$ catalyst still exhibits a high performance of the maximum NO conversion about 85% at 500 °C (*cf.* at the same temperature, 66%

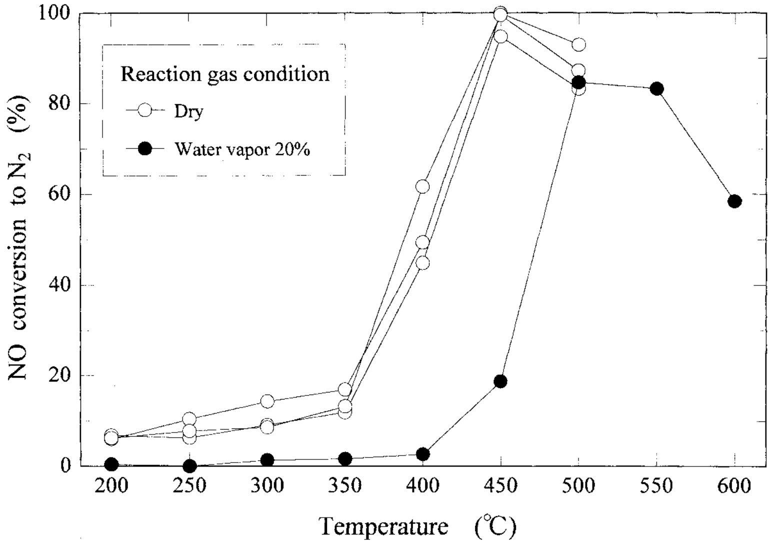

Figure 5. Effect of the water vapor in the feed gas on NO reduction to N$_2$ over 0.5 wt% Co/Al$_2$O$_3$ catalysts. The conditions are the same as those in figure 3.

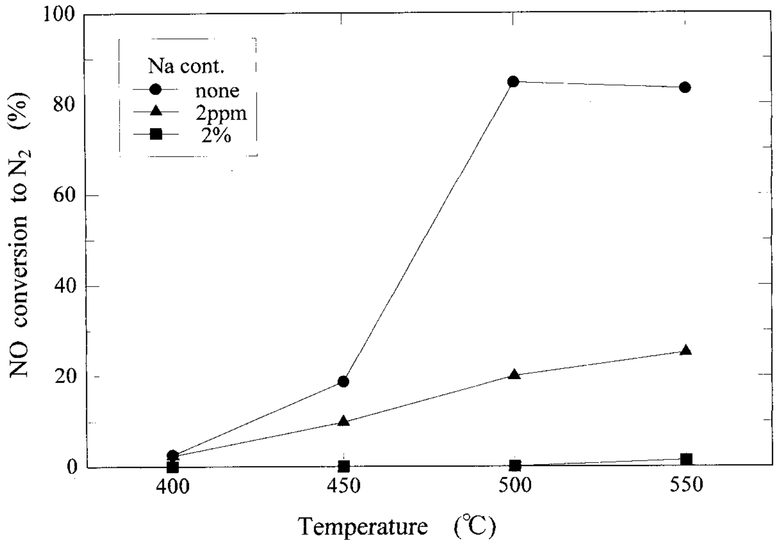

Figure 6. Effect of NaOH added to 0.5 wt% Co/Al_2O_3 catalyst on NO reduction to N_2. The conditions are the same as those in figure 3.

of NO conversion under the H_2O concentration of 8% [8]). It is thus concluded that a high performance catalyst for selective NO reduction with propene can be obtained from the combination of cobalt acetate with the TM-100 alumina even in the presence of excess oxygen and water. The high-purity TM-100 alumina may be primarily responsible for such a high performance. It is known that the sol-gel preparation provides high-purity alumina, by which the cobalt oxide catalyst supported on the alumina exhibited quite a high performance for selective NO reduction with propene [8]. Figure 6 shows the effect of NaOH on the performance of the 0.5 wt% Co/Al_2O_3 catalyst. It is obvious that NO conversion markedly decreases upon adding a small amount of NaOH (2 ppm), which supports our assumption that a high-performance SCR catalyst needs a high-purity alumina support.

High-performance Co/Al_2O_3 catalyst was also prepared by a sol-gel method, where it was reported that the optimal amount of cobalt oxide was larger than that in an impregnation catalyst [6,9]. It is considered that a sol-gel method provides a more uniform mixing of cobalt species with alumina than an impregnation method. As a result, $CoAl_2O_4$ spinel is readily formed or a considerable part of cobalt oxide is included into the alumina matrix and, thereby, a larger amount of cobalt oxide is necessary to produce active sites for selective NO reduction with propene. This is a possible explanation for the difference in the optimal level Co loading between an impregnation catalyst and a sol-gel catalyst.

It was proposed that octahedral Co^{2+} ions dispersed on the alumina surface were active sites of Co/Al_2O_3 catalyst for the selective reduction of NO with hydrocarbons in the presence of excess oxygen [6]. In our 0.5 wt% Co/Al_2O_3 catalyst, Co species other than $CoAl_2O_4$ spinel is evidently present, although no UV–vis absorption typical for Co^{2+} ions in octahedral coordination has been obtained. It is therefore considered that such Co species should produce the active sites for the selective reduction of NO with propene in the presence of excess oxygen.

In conclusion, for selective NO reduction with propene in the presence of excess oxygen, a high performance Co/Al_2O_3 catalyst with an extremely low Co loading of 0.5 wt% was prepared by an impregnation method using a high-purity alumina and Co(II) acetate salt.

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