Enhancing the $NO/C_3H_8/O_2$ Reaction by Using H_2 over Ag/Al_2O_3 Catalysts under Lean-Exhaust Conditions

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We examine the effect of H_2 on the selective reduction of NO by C_3H_8 over Ag/Al_2O_3 catalysts under lean-exhaust conditions. The NO reduction activity caused by C_3H_8 at low temperature (590-760 K) is greatly increased by adding H_2 in the presence of excess oxygen and water vapor.

The emission of nitrogen oxides (NOx) from stationary and automotive engines causes serious environmental problems. Extensive research has been done on reducing NOx using catalysts under lean-exhaust conditions.[1] The effectiveness of silver-alumina catalysts (Ag/Al_2O_3) at reducing NOx by hydrocarbons in an oxidizing atmosphere was first reported by Miyadera and Yoshida.[2,3] The activity and durability of Ag/Al_2O_3 catalysts were demonstrated by using an exhaust gas from a stationary lean-burn gas engine at 763 K.[4] However, the low-temperature activity of Ag/Al_2O_3 catalysts needs to be improved because an acceptable level of deNOx activity by light hydrocarbons contained in the exhaust gases has not been achieved at relatively low temperatures of around 673 K. The reduction of NO by oxygenated organic compounds like alcohols or aldehydes as the reductant has been performed at relatively low temperatures over Ag/Al_2O_3 catalysts.[2,5] Using higher hydrocarbons as the reductant also improved the low-temperature activity.[6] It is desired to improve the low-temperature activity of Ag/Al_2O_3 catalysts for the reduction of NO by the light hydrocarbons. H_2 is a very effective reductant of NO over noble metal catalysts at low temperatures.[7] Even in an oxidizing atmosphere, the NO reduction has been performed by H_2 at low temperatures.[8] Therefore, H_2 is a potential component of NO reduction at low temperatures. However, no work has been reported on the effect of using H_2 to reduce NO in the presence of hydrocarbons. This study investigates the coexistence effect of H_2 and C_3H_8 on the lean NOx reduction over Ag/Al_2O_3 catalysts at low temperatures.

The Al_2O_3 used in this study was obtained by the calcination of commercial high-purity boehmite at 873 K for 3 h. The specific surface area of the obtained Al_2O_3 was 189 $m^2\ g^{-1}$. The Ag/Al_2O_3 catalyst was prepared by impregnating the Al_2O_3 to the incipient wetness with $AgNO_3$ aqueous solution. After drying overnight at 393 K, it was heated at 2 K min^{-1} from 393 K to 873 K and held at 873 K for 3 h in air. The Ag content was adjusted to 2 wt%. The catalysts were sieved to obtain particles of 0.36-0.71 mm. The catalytic activity was measured using a typical fixed-bed flow reactor. A mixture of reaction gas contained 91 ppm NO, 91 ppm C_3H_8 (273 ppm hydrocarbon: C1 basis), 9.1% O_2, 0-1818 ppm H_2, and 9.1% H_2O in He. The total flow rate was 3300 $cm^3\ min^{-1}$ over 1.5-9.0 cm^3 (0.8-4.1 g) of catalysts (GHSV 132000-22000 h^{-1}). After reaching a steady state, the effluent gas was analyzed by a chemiluminescence NOx analyzer and a gas chromatograph. The NOx conversion was calculated on the basis of the differences between the inlet and outlet NOx ($NO+NO_2$) concentrations. It was confirmed that the major product from the NO reduction was N_2 and that a slight amount of N_2O (0-3 ppm) was also formed in all runs.

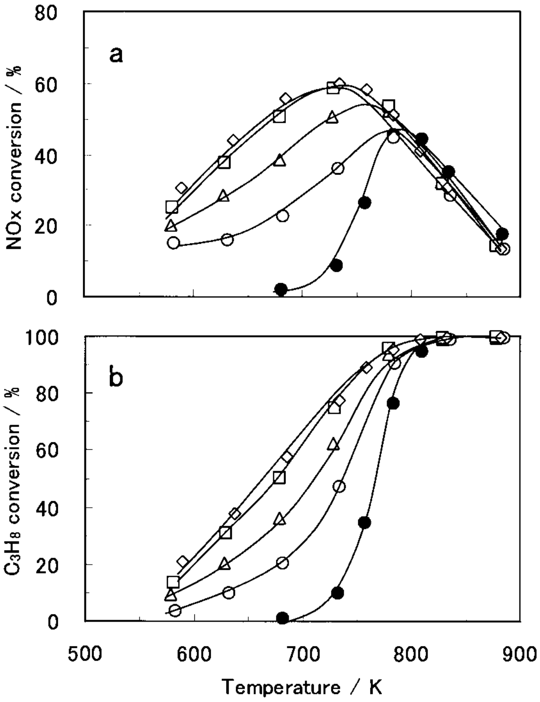

Figure 1. NOx and C_3H_8 conversions over Ag/Al_2O_3 at various H_2 concentrations. Feed: 91 ppm NO, 91 ppm C_3H_8, 9.1% O_2, 9.1% H_2O, and (●) 0 ppm, (○) 227 ppm, (△) 451 ppm, (□) 909 ppm, or (◇) 1818 ppm H_2. GHSV = 44000 h^{-1}.

Figure 1a shows the NOx conversions over Ag/Al_2O_3 in various H_2 concentrations up to 1818 ppm. Closed symbols indicate the NOx conversions in the absence of H_2 in the reaction gas. A NOx conversion of over 30% was achieved only in the narrow temperature range of 760 K to 850 K, and a maximum NOx conversion of 45.6% was achieved at 783 K. When H_2 was added to the reaction gas, the NOx conversion at relatively low temperatures was greatly increased. Increasing the H_2 concentration increased the NOx conversion. In the presence of 909 ppm of H_2, a NOx conversion of over 30% was achieved at temperatures between 590 K and 840 K, and a maximum NOx conversion of 59.9% was achieved at 729 K. However, NO was reduced only a little by the H_2 in the absence of C_3H_8 over the Ag/Al_2O_3 (result not shown). Figure 1b shows the C_3H_8 conversions to COx over Ag/Al_2O_3 in the presence and absence of H_2. Propane light-off occurred at 732 K with com-

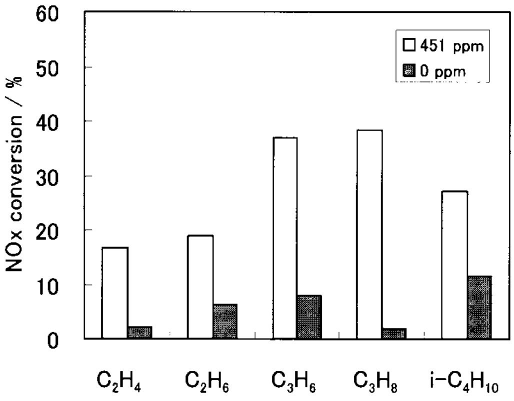

Figure 2. NOx conversion over Ag/Al_2O_3 at 673 K using various hydrocarbons as a reductant in the absence or presence of H_2. Feed: 91 ppm NO, 273 ppm HC (C1 basis), 9.1% O_2, 9.1% H_2O, and 0 or 451 ppm H_2. GHSV = 44000 h^{-1}.

plete conversion at 834 K in the absence of H_2. When H_2 was added to the reaction gas, the light-off temperature of C_3H_8 was lowered; however, the temperature of the complete conversion was not changed. The light-off temperature of C_3H_8 in the C_3H_8/O_2 reaction was also lowered by adding H_2 (result not shown). Since the temperature region for the NOx reduction is closely related to that for hydrocarbon oxidation,[9] the NOx was clearly reduced by C_3H_8 at low temperatures. This indicates that the $NO/C_3H_8/O_2$ reaction continues at low temperatures and over a wide temperature range because of the presence of H_2 in the reaction gas. Figure 2 shows the NOx conversion over Ag/Al_2O_3 at 673 K when various light hydrocarbons are used as the reductant in the presence and absence of H_2. The NOx conversion was also increased by adding H_2 when every hydrocarbon was used as the reductant.

Figure 3 shows the effect of gas hourly space velocity (GHSV) in the $NO/C_3H_8/O_2$ reaction. The dependence of GHSV on the NOx conversion is compared at 773 K over Ag/Al_2O_3 in the presence and absence of H_2. The NOx conversion in the presence of H_2 stayed constant under a high GHSV of more than 100000 h^{-1}, while the NOx conversion greatly decreased with an increase in the GHSV in the absence of H_2. This indicates that the NOx reduction rate in the presence of H_2 is much faster than that in the absence of H_2. Therefore, it is suggested that the rate-determining step for the NO reduction by C_3H_8 is accelerated by using H_2 over Ag/Al_2O_3.

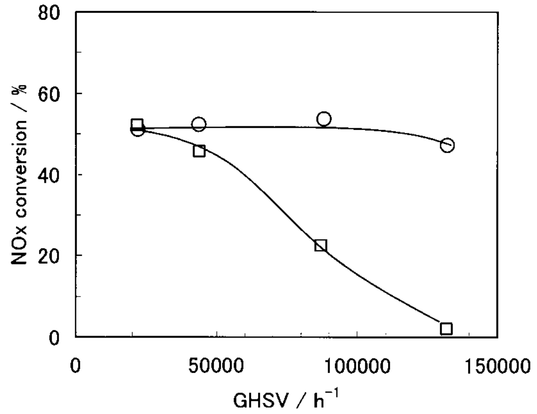

Figure 3. Dependence of GHSV on the NOx conversion over Ag/Al_2O_3 at 773 K with 0 ppm (□) or 451 ppm (○) of H_2. Feed: 91 ppm NO, 91 ppm C_3H_8, 9.1% O_2, 9.1% H_2O, and 0 ppm or 451 ppm H_2.

In summary, adding H_2 significantly produced the NOx reduction by light hydrocarbons at low temperatures. These findings show that NOx can be greatly reduced in many kinds of exhaust gases from lean-burn engines. A mechanistic study of the effect of H_2 will be done in the future.

References and Notes

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