Enhanced De-NO_x Performance of Ag-Al_2O_3 Catalyst by Increasing Carbon Number of Hydrocarbon Reductants

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(Received July 14, 1999; CL-990622)

A significant effect of carbon number on the catalytic property was observed for the selective reduction of NO by *n*-alkanes over Ag-Al_2O_3 catalyst; the higher alkanes as the reductant resulted in the higher activity and the higher water-tolerance.

The selective reduction of NO by hydrocarbons (HC-SCR) in the presence of excess oxygen is a potential method to remove NOx from various exhausts, such as diesel engines exhausts.[1,2] However, although a number of catalysts, such as Cu- and Co-ZSM-5, have been tested in the HC-SCR, to date no catalyst seems to be suitable for the diesel de-NO_x conditions. Although alumina- supported silver catalysts (Ag/Al_2O_3), which have high tolerance to water and SO_2, can be one of the candidates for practical use,[3] a relatively high temperature for achieving NO reduction is a problem to be solved. In addition, the catalysts are required to effectively use higher hydrocarbons, which are already present in diesel fuel and emissions. However, most of the studies on HC-SCR have been conducted using lower hydrocarbons as the reductant,[1,2] and few works have focused on the effect of increasing carbon number[4,5] or the use of higher hydrocarbons as the reductant.[6] Here, we report a systematic study of the carbon number effect on de-NO_x activity over Ag-Al_2O_3 catalyst. When higher alkanes are used, significant improvements of both low temperature activity and water-tolerance are observed.

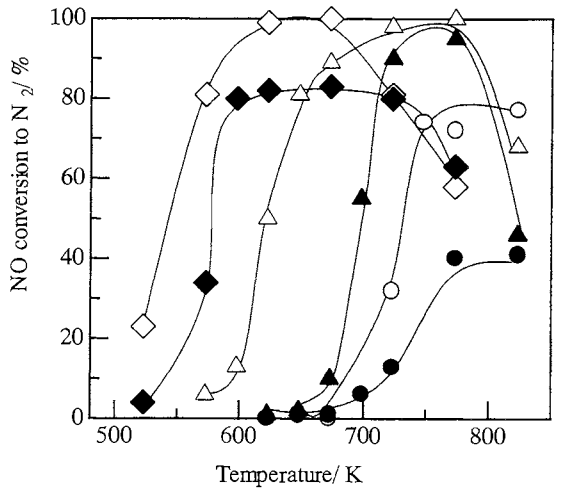

Figure 1. NO conversion to N_2 on Ag-Al_2O_3 catalyst using various *n*-alkanes: (●) methane, (○) ethane, (▲) propane, (△) *n*-butane, (◆) *n*-hexane, (◇) *n*-octane. Conditions: NO= 1000 ppm, HC= 6000 ppm C, O_2= 10%, H_2O= 2%, and W/F= 0.12 g s ml^{-1} except for methane-SCR (W/F= 0.9 g s ml^{-1}).

The Ag-Al_2O_3 catalyst (Ag content= 2 wt%, surface area= 190 m^2 g^{-1}) was prepared by hydrolysis of a mixed solution of aluminum triisopropoxide dissolved in ethanol and silver nitrate dissolved in ethylene glycol. The precipitate obtained was filtered and dried at 393 K for 12 h and then calcined at 1073 K for 4 h. The alumina-supported silver catalyst (Ag/Al_2O_3) with Ag content of 2 wt% was prepared according to the method by Miyadera et al.[3] The catalytic test was performed with a flow reactor by passing a mixture of 1000 ppm NO, 6000 ppm C of hydrocarbon, 10% O_2 and 0 or 2% H_2O in helium at a rate of 100 cm^3 min^{-1} over 0.02-0.9 g catalyst. Liquid hydrocarbons (C6 ~C8) were introduced by passing part of the carrier gas to the saturator. After reaching steady-state, effluent gas was analyzed by gas chromatography and chemiluminescence NO_x analyzer.

Figure 1 compares the NO conversion on Ag-Al_2O_3 when various linear alkanes (from methane to *n*-octane) are used as a reductant. Clearly, the carbon number in the *n*-alkane reductant significantly affects NO reduction activity. As carbon number increased, the temperature range at which NO reduction occurs shifted to the lower temperature region. Light-off temperature for hydrocarbon conversion to CO_x ($CO+CO_2$) also shifted to the lower temperature with increase in the carbon number (result not shown). It should be noted that the similar results were obtained for Ag/Al_2O_3, though the NO reduction activity was lower than Ag-Al_2O_3. The reaction rates at 623 K were measured under the condition where the conversions were below 60% and plotted in Figure 2 as a function of the carbon number. As the carbon number increased from 1 to 8, the formation rates of N_2 and CO_x increased in a similar manner (by a factor of 10^3-10^4). The rate of hydrocarbon oxidation by O_2 (in the absence of NO) also increased as the carbon number increased. Considering the fact that the mean energy of one C-H bond decreases as the carbon number in *n*-alkanes increases,[7] there seems to be a link between the reactivity of the hydrocarbon molecule and the catalytic activity for NO reduction. By assuming that hydrocarbon activation is one of the key steps in HC-SCR,[8] one interpretation of the above results is that as the number of carbon atoms in *n*-alkanes increases, the reactivity of hydrocarbon increases, and as a result, the formation rate of N_2 and CO_x increases. In a previous review by Shelef, it was stated, on the basis of the report by Witzel et al.[5] that the same specific activity for HC-SCR is obtained for a wide array of reductants, that the activation of the reductant is not the limiting step while the oxidation of NO to NO_2 probably is.[2] However, results in the present study suggest that the activation of the reductant is the important step and may be involved in the rate-limiting step of HC-SCR on Ag-Al_2O_3.

Figure 2 includes the ratio of the reaction rates in the presence of water vapor to those in the absence of water vapor. For lower alkanes as a reductant, inhibition of the reaction by water vapor was observed as reported for most of the HC-SCR catalysts. However, the degree of activity suppression decreased

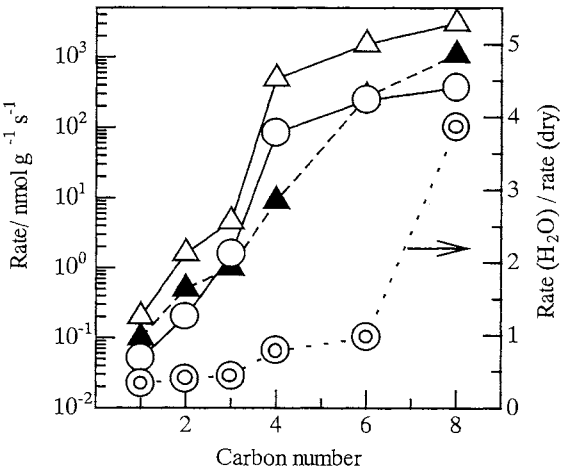

Figure 2. Rates of (○) N_2 and (△) CO_x formation in SCR reaction and rate of (▲) CO_x formation in HC+O_2 reaction on Ag-Al_2O_3 at 623 K as a function of carbon number in *n*-alkanes. ◎ denotes the ratio of the N_2 formation rate in the presence of water to that in the absence of water. Conditions: NO= 0 or 1000 ppm, HC= 6000 ppm C, O_2= 10%, H_2O= 2%, and W/F= 0.01 ~0.9 g s ml^{-1}.

as the carbon number increased. For *n*-octane as a reductant, in contrast, the activity was markedly increased by water vapor, which is similar to the results reported in several C_3H_6-SCR systems.[9] Taking into account the fact that the adsorption enthalpy increases with carbon number of *n*-alkanes,[10] the higher alkane as a reductant may result in the less inhibition of hydrocarbon adsorption by competitive water adsorption, which leads to the higher water-tolerance. Possible reasons of the promoting effect by water in the case of *n*-octane is considered to be, according to the proposals in C_3H_6-SCR systems,[9] the suppression of the poisoning effect caused by strongly adsorbed hydrocarbon species or the removal of these species by H_2O.

In summary, significant hydrocarbon effects were observed for NO selective reduction by *n*-alkanes on Ag-Al_2O_3 catalyst. The higher de-NO_x activity and the higher water-tolerance are obtained when the higher alkanes are used as a reductant. Although the real diesel exhaust contains much higher hydrocarbons (C10~C25),[11] the present results will provide a direction for obtaining high de-NO_x performance under diesel exhaust conditions.

K. S. acknowledges support by the Fellowship of JSPD for Japanese Junior Scientists.

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