Promoting Effect of Water Vapor on the Catalytic Activity of Cobalt-Exchanged MFI Zeolite for the Selective Reduction of NO by C_3H_8

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The presence of water vapor was found to remarkably enhance the catalytic activity for selective reduction of NO by C_3H_8 over Co^{2+}-exchanged MFI zeolite prepared from H-form MFI zeolite.

Selective catalytic reduction of NO by hydrocarbon (HC-SCR) under excess oxygen has received much attention because of its potential applicability to removal of NO_x from exhaust such as lean-burn gasoline and diesel engines. Since the first report on Cu-ZSM-5,[1,2] a large number of studies have been made on the development of de-NO_x catalysts and many types of catalyst have been reported.[3] Co^{2+}-exchanged zeolites, as firstly reported by Li and Armor,[4] are known to be very active for the SCR of NO by lower alkane (CH_4[4,5] and C_3H_8[6]). However, their catalytic activity is strongly inhibited by the coexistence of water vapor, which is a serious concern for the development of these materials for practical purposes.[5,6] A few examples of the promoting effect of water vapor on the HC-SCR activity have been reported on some of catalysts by using C_3H_6,[7,8] *iso*-C_4H_{10},[9] and *n*-octane[10] as a reductant. In the case of lower alkane as a reductant, however, the promoting effect of water vapor has so far not been known.

In this paper, we will show the effect of water presence on the C_3H_8-SCR activity greatly depends on Co^{2+} exchange level in zeolite and the coexisting cation. Interestingly, over Co^{2+}-exchanged MFI zeolite having less than 100% of Co^{2+} exchange level prepared from H-form MFI zeolite, it was found that the presence of water vapor remarkably enhances the catalytic activity for the selective reduction of NO by C_3H_8.

H-MFI (Si/Al = 22) zeolite, which was supplied by Tosoh Co., were used as the parent zeolite. Na-MFI was obtained by exchanging H^+ with Na^+ in an aqueous solution of sodium acetate at 353 K. Co^{2+}-exchanged MFI catalysts were prepared from H-MFI or Na-MFI by ion-exchange with an aqueous solution of cobalt(II) acetate at 353 K.[11] After filtration, the sample was washed with distilled water and dried at 393 K, followed by calcined at 773 K for 6 h in flowing dried air. If necessary, the exchange was repeated two to three times before washing to reach high Co^{2+} loading. The final samples were analyzed by inductively coupled plasma emission spectroscopy (ICP, Jarrel-Ash MODEL 975) to determine their elemental composition. Hereafter, the catalysts will be designated as Co-starting form of zeolite (cobalt exchange level), e.g., CoH-MFI(70). The catalyst was pretreated in flowing 20% O_2/He at 773 K for 1 h. The catalytic test was performed with a fixed-bed flow reactor at atmospheric pressure by passing a mixture of 1000 ppm NO, 2000 ppm C_3H_8, 6.7% O_2 and 0 or 2% H_2O in He at a rate of 100 cm^3 min^{-1} over 0.10 g of catalyst. After reaching a steady-state, the effluent gas was analyzed by a gas chromatograph and a chemiluminescence NO_x analyzer.

Figure 1 shows the effect of water vapor on the catalytic activity of CoH-MFI(70) zeolite for the selective reduction of NO by C_3H_8. Above 673 K, the presence of water vapor has no effect on the catalytic activity. Below 673 K, on the other hand, it was found that the presence of water vapor remarkably enhances the catalytic activity.

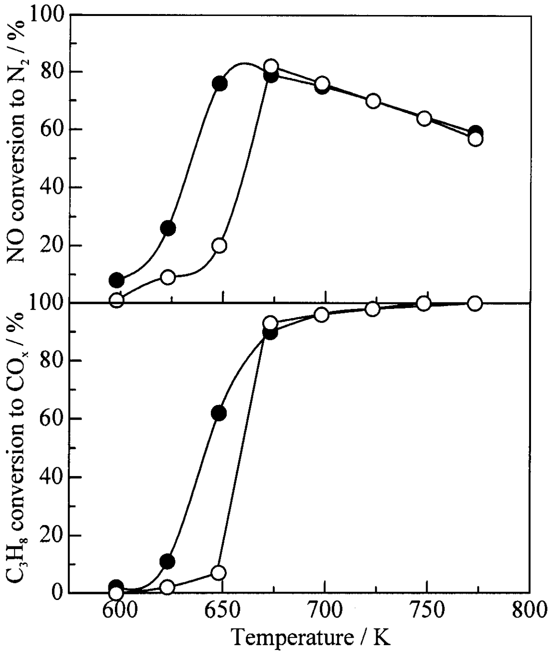

Figure 1. Effect of water vapor on the catalytic activity of CoH-MFI(70) zeolite for the selective reduction of NO by C_3H_8. NO, 1000 ppm; C_3H_8, 2000 ppm; O_2, 6.7%; H_2O, 0%(○) or 2%(●); He, balance; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.10 g.

The promoting effect of water vapor on NO reduction by C_3H_8 was further investigated on catalysts with different Co^{2+} exchange level prepared from different form of zeolite (H- or Na-form MFI). Figure 2 shows the time dependence of NO conversion to N_2 at 648 K over CoH-MFI(58), CoH-MFI(70), CoH-MFI(118) and CoNa-MFI(72), respectively. In the initial run for 150 min without water, the rapid decrease in NO conversion was observed over CoH-MFI(58) and CoH-MFI(70), and after that the NO conversion gradually decreased with time-on-stream. As shown in the following 90-min run with 2% water, the NO conversions over CoH-MFI(58) and CoH-MFI(70) were greatly enhanced and were stable in the presence of water. After that, again by eliminating water from the reactant feed, the catalytic activities decreased the same as initial run. These results indicate that the catalyst is reversibly deactivated in the absence of water so that the activity is recovered by addition of water vapor. In contrast, the catalytic activities of CoH-MFI(118) and CoNa-MFI(72) were suppressed by addition of water vapor, although the catalytic activities immediately recovered by eliminating water vapor from the reactant feed. Furthermore, the catalytic activities were stable in the absence of water vapor. These results indicate that water reversibly inhibits the reaction over these catalysts, which is completely contrary to the promoting effect over CoH-MFI(58) and CoH-MFI(70). This difference in the effect of water vapor is not due to Co^{2+} exchange level, because CoH-MFI(70) and CoNa-MFI(72) have almost the same Co^{2+} content. The presence of H^+ site may be responsible for this promoting effect of water vapor.

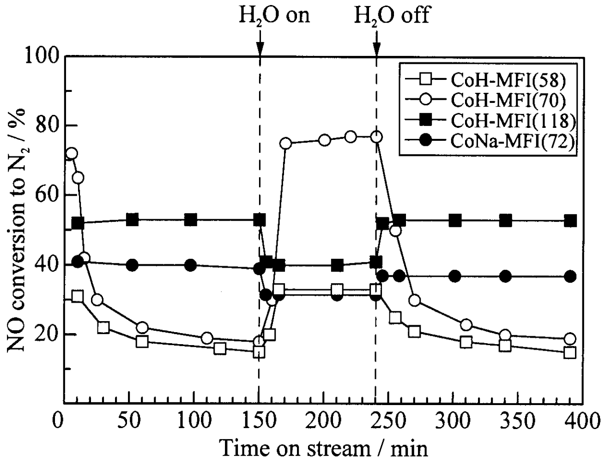

Figure 2. Time dependence of catalytic activity for NO reduction by C_3H_8 at 648 K over Co-exchanged MFI zeolite. NO, 1000 ppm; C_3H_8, 2000 ppm; O_2, 6.7%; H_2O, 0 or 2%; He, balance; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.10 g.

The reason for the decrease in catalytic activity by addition of water vapor, which was observed on CoH-MFI(118) and CoNa-MFI(72), should be the reaction inhibition due to the competitive adsorption between NO and H_2O.[5,6] Tabata et al. reported similar results that the inhibiting effect of water vapor was observed in the C_3H_8-SCR over CuH-MFI(106) and CoH-MFI(111).[6] To our knowledge, however, the promoting effect of water vapor on the HC-SCR activity has so far not been reported with using lower alkane as a reductant, and therefore, the promoting effect observed over CoH-MFI(58) and CoH-MFI(70) is very interesting. A few examples of enhanced NO reduction activity by addition of water vapor have been reported with using C_3H_6,[7,8] *iso*-C_4H_{10}[9], and *n*-C_8H_{18}[10] as a reductant. These promoting effects can be considered that water vapor suppresses the formation of carbonaceous materials and/or promotes the removal of carbonaceous materials deposited on the catalyst surface.[7–10] Although such explanations can be applied to the promoting effect observed in the present case, the color change of catalyst into brown or black as usual observed in the formation of carbonaceous materials was not found at all after the reaction test on each catalysts. Therefore, the inhibiting materials may not be carbonaceous materials, but the strongly adsorbed reaction intermediates on catalyst surface, possibly on H^+ site.

In conclusion, the effect of water vapor on the catalytic activity of Co^{2+}-exchanged MFI zeolite for the selective catalytic reduction of NO by C_3H_8 remarkably depends on the Co^{2+} exchange level and coexisting cation. The promoting effect of water vapor on NO reduction activity was found over Co^{2+}-exchanged MFI zeolite having less than 100% of Co^{2+} exchange level prepared from H-form MFI zeolite, while the inhibiting effect of water vapor was found over Co^{2+}-exchanged MFI zeolite having excess Co^{2+} exchange level or prepared from Na-form MFI zeolite.

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