Catalysis Letters 45 (1997) 267–269

Low-temperature selective reduction of NO with propene over alkaline-exchanged mordenites

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Received 7 December 1996; accepted 7 March 1997

Partially protonated alkaline mordenites showed higher activity per acid amount below 573 K than acidic zeolites for the selective reduction of NO with C_3H_6 in the presence of O_2, which can be related to a high concentration of NO_3^- species in the zeolite channels.

Keywords: selective reduction of NO, propene, mordenite, alkaline-exchange, low-temperature activity, role of nitrate, promoting effect

Much attention has been paid to the removal of nitrogen oxides (NOx) from exhaust by selective catalytic reduction with hydrocarbons over ion-exchanged zeolites, such as Cu/ZSM-5 [1,2], Ce/ZSM-5 [3], Ga/ZSM-5 [4], Co/ZSM-5 [5], and so on. These ion-exchanged zeolites are very active for the reduction of NO; however, there are still some problems for the design of active catalysts for practical use [6]. The development of a catalyst which is active in a wide range of temperatures is one of the targets; especially, enhancement of the catalytic activity at low temperature is desired.

We have previously reported [7] a linear correlation between the activity for the reduction of NO and the amount of strong acid sites over acidic zeolites which exhibit the activity only at high temperature. In the present letter, we describe a unique catalytic behavior of alkaline-exchanged mordenites, i.e., a significant promoting effect of incorporated alkaline cations on the activity for the reduction of NO with C_3H_6 at low temperature, which suggests a possibility of lowering the reaction temperature of the removal of NOx.

H-mordenite and Na-mordenite were Reference Catalysts of the Catalysis Society of Japan (JRC-Z-HM10 and JRC-Z-M10) of which the SiO_2/Al_2O_3 ratio was 9.9. For the preparation of Na–H-mordenite, Na-mordenite as received was at first fully ion-exchanged with Na^+ in aqueous solution of $NaNO_3$ for three times. Li-mordenite and K-mordenite were prepared from H-mordenite by ion-exchange with acetate solutions. These alkaline-exchanged mordenites were then partially protonated with NH_4NO_3 solution. The $NO–C_3H_6–O_2$ reaction was carried out in a conventional continuous-flow apparatus at atmospheric pressure. A mixture of 940 ppm NO, 288 ppm C_3H_6 and 6.6% O_2 diluted with He was fed to 1.5 g or 0.5 g of catalysts at a flow rate of 42.2 $cm^3\ min^{-1}$ ($SV = 1200$ or $3600\ h^{-1}$). A steady state activity was measured after pre-adsorption of NO and C_3H_6 followed by the exposure of the catalysts to the feed gas for 3–24 h so as to obtain a good carbon balance. The alkaline-exchanged mordenites were not deactivated for more than 10 h. IR spectra were measured with a JASCO FT/IR-5 equipped with a quartz cell connected to a conventional high-vacuum system. NH_3-TPD (temperature-programmed desorption) spectra were measured as reported previously [7,8].

Figure 1 shows the activity of various zeolites for the $NO–C_3H_6–O_2$ reaction at 573 K as a function of acid amount. In the case of acidic zeolites such as H-form zeolites (H-mordenites and H-ZSM-5) with various SiO_2/Al_2O_3 ratios and H-mordenites partially ion-exchanged with Ca, Sr, Ba, Ga and La [7] (open circles), the activity for NO reduction is proportional to the acid amount determined by the NH_3-TPD method. Closed symbols represent the relation observed on partially protonated alkaline-exchanged mordenites. In these cases, the amount of acid sites is shown by an error bar: the lowest value corresponds to the amount measured by using NH_3-TPD, symbols to the amount of loaded NH_4NO_3 in the starting solution for the ion-exchange, and the highest value corresponds to that estimated from the amount of alkaline cations by the inductive-coupled plasma method. The activity of Li–H-, Na–H-, and K–H-mordenite also increased with the acid amount, indicating that the acid amount is one of the factors controlling the activity of these zeolites. It should be noted that the activities of partially protonated alkaline mordenites

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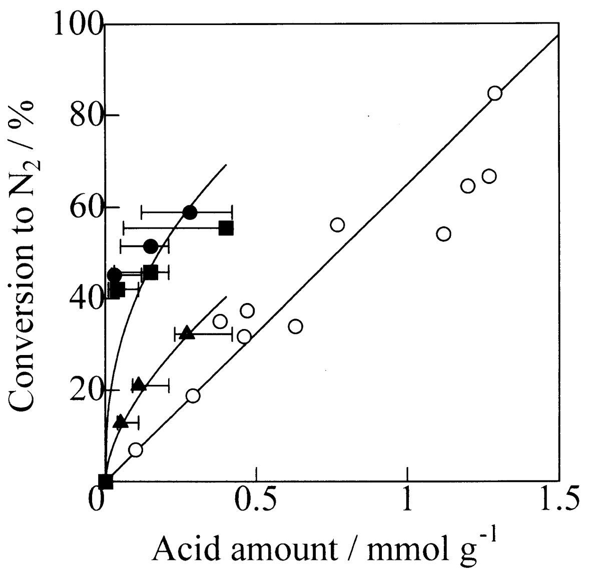

Figure 1. Catalytic activity of partially protonated Li–H- (●), Na–H- (■) and K–H-mordenite (▲) as compared with acidic zeolites (○). Reaction temperature was 573 K and space velocity was 3600 h^{-1} for all the catalysts.

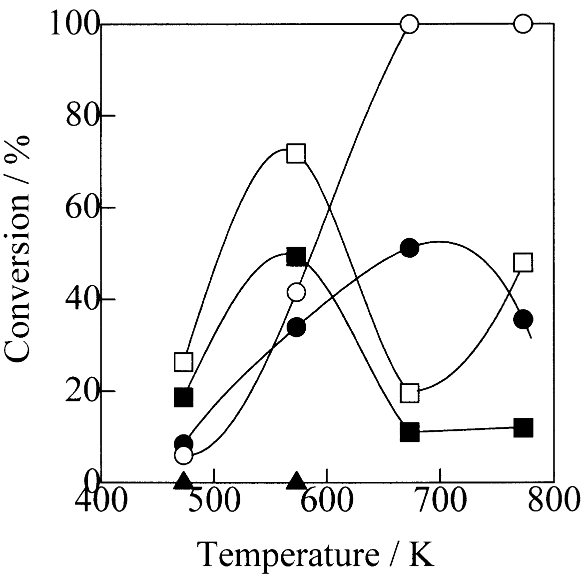

Figure 2. Catalytic activity of H-mordenite (●, ○), Na-mordenite (■, □) and Na(105)-mordenite (▲, △) as a function of reaction temperature. Closed symbols and open symbols represent the conversion of NO and C_3H_6, respectively. Space velocity was 3600 h^{-1} for H-mordenite and 1200 h^{-1} for Na-mordenite and Na(105)-mordenite.

are significantly higher than those of acidic zeolites at the same acid amount. The activity of K–H-mordenites was lower than those of Li–H- and Na–H-mordenites, indicating that K^+ has a less appreciable promoting effect. When excess Na was introduced into Na-mordenite to obtain a Na-exchange level of 105% (Na(105)-mordenite), NO and C_3H_6 were not converted (acid amount = 0 in figure 1), indicating that the acid sites are indispensable to this reaction, and the role of Na^+ ions seems to promote the catalytic activity of acid sites. Turnover frequencies based on the acid amount were about 1×10^{-4} s^{-1} for Li–H- and Na–H-mordenites and 2×10^{-5} s^{-1} for acidic zeolites, respectively. A similar promoting effect of alkaline cations was observed at 473 K, though, at 673 K, both alkaline-containing and acidic zeolites showed the same activity at the same acid amount. This promotion effect of alkaline cations may be related to the high activity of Na–Fe-ZSM-5 at lower reaction temperature, as reported by Teraoka et al. [9]. By using received Na-mordenite (JRC-Z-M10) as a typical example, the promoting effect of alkaline cations at lower temperature was examined.

Figure 2 shows the temperature dependence of the conversion of NO and C_3H_6 over H-mordenite and Na-mordenite. In the case of H-mordenite, the conversion of NO increased with the reaction temperature up to 673 K, and then decreased with further increase in the reaction temperature. Conversion of C_3H_6 was complete above 673 K, suggesting the decrease in the conversion of NO at higher temperature is due to non-selective oxidation of C_3H_6 by O_2 [7,9]. In the case of Na-mordenite, the maximum activity for the reduction of NO was observed at lower temperature, i.e., 573 K. Conversion of NO and C_3H_6 significantly decreased at 673 K, and only oxidation of C_3H_6 by O_2 increased again at 773 K. Since the conversion of C_3H_6 at 673 K was not complete, the decrease in the reduction of NO at higher temperature is not due to the consumption of C_3H_6 as a reducing reagent.

In the separate experiments, Na-mordenite exhibited no activity for C_3H_6 oxidation with O_2, though H-mordenite was active for this reaction. This result indicates that Na^+ ion is not effective for the activation of C_3H_6. Another possibility of promotion effect of Na^+ ion may be related to an activation of NO.

Figure 3 shows IR spectra of adsorbed species on Na-mordenite and H-mordenite after NO–O_2 reaction for 2 h followed by the evacuation at 573 K for 10 min. In the case of Na-mordenite, a strong absorption band was observed at 1394 cm^{-1}. The spectrum agreed with that of $NaNO_3$, and the band can be assigned to $\nu(NO_2)$ of NO_3^- species [10] adsorbed on exchanged Na^+ ion. As shown in figure 3b, this band decreased significantly at 673 K, which corresponds with the fact that the decomposition temperature of $NaNO_3$ is 653 K [11]. In the case of H-mordenite, on the other hand, no absorption band was observed in the IR spectrum after NO–O_2 reaction. The behavior of the band was quite in agreement with that of the catalytic activity shown in figure 2: The activity of Na-mordenite was higher at 573 K than that at 673 K, but H-mordenite was less active at 573 K. These results suggest that the unique temperature dependence of Na-mordenite can be related to the high concentration of NO_3^- species in the zeolite channels at lower temperature, or, in other words, the promotion effect of

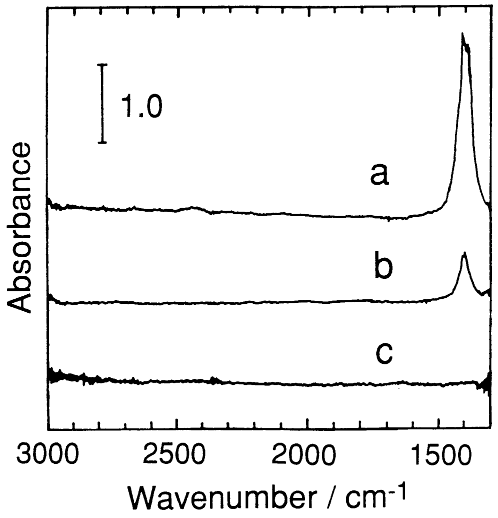

Figure 3. IR spectra of adsorbed species after NO–O_2 reaction over Na-mordenite at 573 K (a), Na-mordenite at 673 K (b) and H-mordenite at 573 K.

alkaline ions arises from the enrichment of NO_3^- species in the zeolite channels.

In conclusion, it was clarified that the alkaline-exchange into acidic mordenite significantly enhances the low-temperature activity for the reduction of NO with C_3H_6, which arises from the formation of NO_3^- species. Further investigation is in progress for the elucidation of the role of NO_3^- species in the promoting effect at low temperature.

Acknowledgement

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan (No. 07242105 and 06555242).

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