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Selective Reduction of Nitrogen Monoxide with Propene over Cu-Silicoaluminophosphate (SAPO) under Oxidizing Atmosphere

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Catalytic activity of Cu-ion exchanged SAPO for NO reduction with C_3H_6 under oxidizing atmosphere was studied. Cu-SAPO-34 exhibits higher activity for NO reduction than Cu-ZSM-5, and the high catalytic activity of Cu-SAPO-34 was sustained up to 600 °C. Furthermore, heat resistance of Cu-SAPO-34 is superior to Cu-ZSM-5.

Selective reduction of nitrogen oxides under an oxidizing atmosphere with hydrocarbons has attracted attention as a process for the catalytic removal of NO in the exhaust gas of diesel or lean-burn engines. The selective reduction of nitrogen oxide by hydrocarbons under an oxidizing atmosphere has been reported over Al_2O_3, SiO_2-Al_2O_3,1,2) metallosilicate,3,4) and zeolite ion-exchanged by Cu,5) H,6) or Ce ion.7) In particular, Cu ion-exchanged zeolite with a pentasil structure is highly active for the selective reduction of NO in the temperature range below 500 °C.5) Silicoaluminophosphate (SAPO), first synthesized by Union Carbide Corp., is a kind of molecular sieve which has an ion exchanging property. In this study, we investigated the catalytic activity of Cu ion-exchanged SAPO for the selective reduction of NO with C_3H_6 under an oxidizing atmosphere.

Three types of SAPO, 5, 11, and 34, were synthesized according to U.S. Patent,8) and have a Si content (Si/(Si+P)) of 0.15. Synthesized SAPO and the reference, ZSM-5 zeolite (Mobil, SiO_2/Al_2O_3=20), were ion-exchanged with Cu in a 0.01 M Cu acetate aqueous solution, and then ammonia water was added for exchanging Cu ion completely. Exchanged amounts of Cu^{2+} were about 3 wt% for each type of SAPO and ZSM-5 according to an analysis with atomic absorption flame emission spectrophotometer. After calcination of the catalysts at 400 °C for 4 h under a He stream, the catalytic activities for NO removal were measured with a fixed bed flow reactor. A mixed gas consisting of NO (5000 ppm), C_3H_6 (1000 ppm), O_2 (5%), and He (remainder) was fed to the catalyst bed at W/F=0.3 g-cat s cm^{-3}, where W and F stand for the catalyst weight and flow rate, respectively. Effluent gases was analyzed by gas chromatography. Heat resistance of SAPO-34 and ZSM-5 were examined by calcinating at a prescribed temperature for 2 h.

Figure 1 shows the catalytic activity of Cu ion-exchanged SAPO and ZSM-5 as a function of reaction temperature. After a slight decrease in catalytic activity within few hours, all catalysts exhibited a steady state conversion. As reported, Cu-ZSM-5 exhibits high activity for NO reduction at 300 °C and the activity decreases with increasing temperature. Although the temperature at which each Cu-SAPO attains maximum conversion into N_2, is higher than that of Cu-ZSM-5 by about 50 °C, the activity of Cu-SAPO for NO reduction is comparable to that of Cu-ZSM-5 except for SAPO-5. In particular, Cu-SAPO-34 exhibits higher activity for NO reduction than Cu-ZSM-5 over the entire temperature range examined. Furthermore, the high activity was sustained up to 600 °C. Therefore, conversion into N_2 is two times higher on Cu-SAPO-34 than Cu-ZSM-5 at 600 °C. Pore structures of SAPO-34 and ZSM-5 are three dimension and those of SAPO-5 and -11 are one dimension. High activity for NO reduction on SAPO-34 and ZSM-5 may suggest the possibility that molecular sieves with three dimentional pore structure are favorable for NO reducive catalysts.

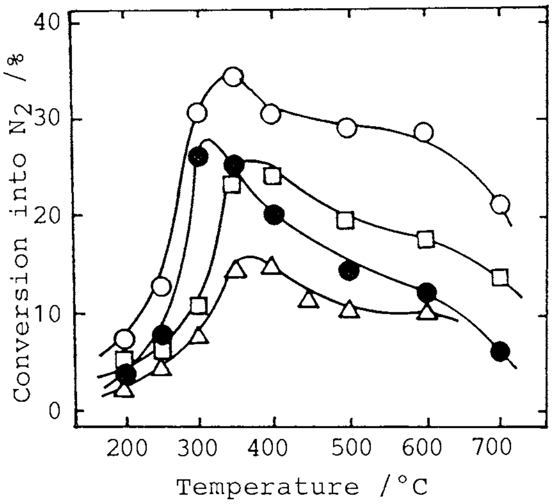

Fig. 1. Temperature dependence of catalytic activity of Cu-ZSM-5 and various types of Cu-SAPO for NO reduction with C_3H_6.

○ SAPO-34 □ SAPO-11 △ SAPO-5
● ZSM-5

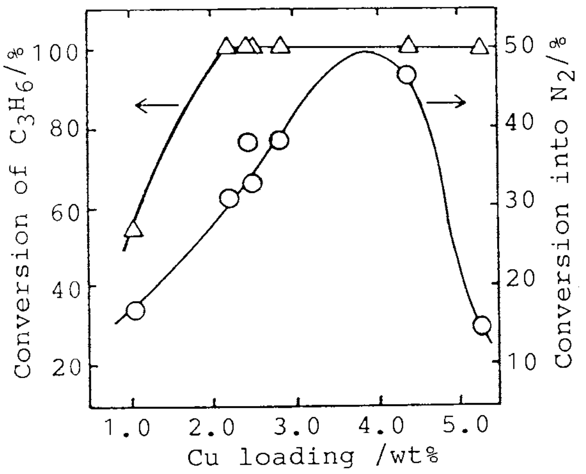

Fig. 2. Conversion into N_2 and C_3H_6 conversion at 350 °C on Cu-SAPO-34 as a function of Cu loading.

Conversion into N_2 at 350 °C on Cu-SAPO-34 is plotted against Cu loading in Fig. 2. The amount of ion exchange sites present in SAPO is theoretically equal to the content of Si atoms. However, the amount of ion exchange sites does not relate simply to the amount of Si when the Si content is high. At the high Si content, a pair of lattice Al and P atoms are substituted by two Si atoms and thus no additional ion exchange sites will be formed despite the increase of Si content. Therefore, the amount of ion-exchanged Cu in this study was expressed on the basis of weight (Fig. 2). Since the number of active sites for NO reduction increase with increasing Cu exchange level, conversion into N_2 increased with increasing Cu ion exchange level and attained a maximum at the ion-exchange level from 3.0 to 4.0 wt%. Oxidation of C_3H_6 to CO_2 proceeds competitively with the selective reduction of NO with C_3H_6. Considering from C_3H_6 conversion, the excess amount of exchanged Cu ion promotes the simple oxidation of C_3H_6. As a result, the activity for NO reduction decreased with increasing Cu ion-exchange level higher than 4.0 wt%. The optimum exchange level of Cu^{2+} exists in the range from 3.0 to 4.0 wt%.

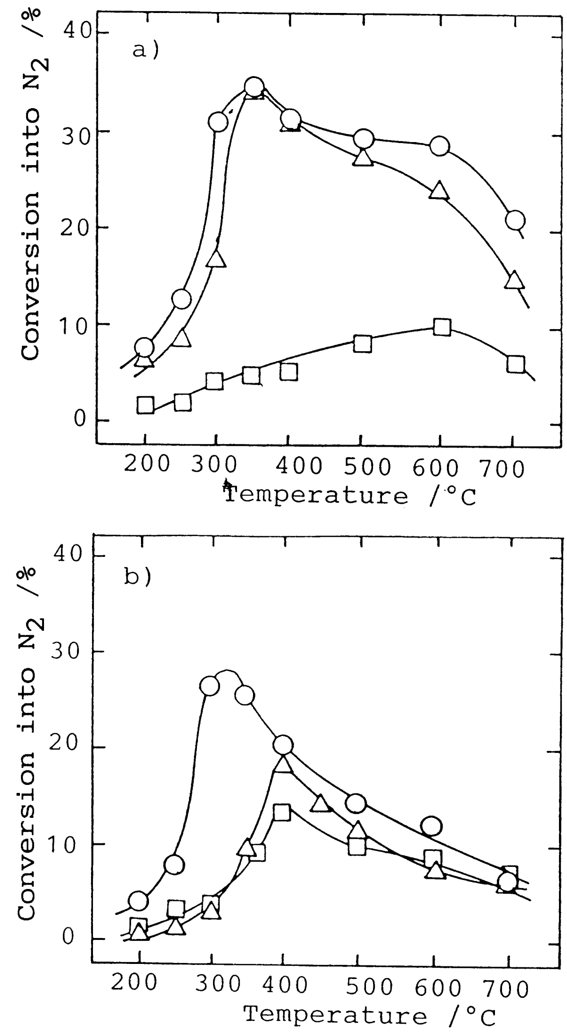

Fig. 3. Effect of heat treatment under dry atmosphere on the activity for NO reduction of (a) Cu-SAPO-34 and (b) Cu-ZSM-5. (Precalcination at ○500 °C, △800 °C, □900 °C.)

Heat resistance is another important characteristic for NO removing catalysts employed for internal-combustion engines. Figure 3 shows the effects of heat treatments on the activity of Cu-SAPO-34 and Cu-ZSM-5 for NO reduction. The color of Cu-ZSM-5 was changed from bright blue to light green and the conversion into N_2 decreased drastically after calcinating at 800 °C. On the contrary, the activity for NO reduction and the color of Cu-SAPO-34 are independent of heat treatment below 800 °C. However, the activity of both catalysts for NO reduction was almost disappeared after calcination at 900 °C. X-Ray analysis of Cu-SAPO-34 and Cu-ZSM-5 revealed that the crystal lattices of both catalysts had been destroyed by calcination at 900 °C. This suggests that the decrease in the catalytic activity for NO reduction resulted from the destruction of the crystal structure and/or the aggregation of Cu ion.

Exhaust gases from engines contain a high concentration of steam. Influence of steam on the heat resistance was further studied for Cu-ZSM-5 and Cu-SAPO-34 (Fig. 4). The heat resistance of both ZSM-5 and SAPO-34 decreased in the presence of ca. 3 vol.% of H_2O. In the case of Cu-ZSM-5, calcinating at 700 °C under dry air has little influence on its activity for NO reduction, but the same heat treatment under wet air drastically decreases the activity. However, the extent of decrease in the activity of Cu-SAPO-34 for NO reduction was relatively small even after calcination at 800 °C under wet air. This suggests that the heat resistance of Cu-SAPO-34 is higher than that of Cu-ZSM-5 under not only dry but also wet atmospheres. This study reveals that SAPO-34 ion-exchanged by Cu exhibits high activity for NO reduction with C_3H_6 under oxidizing atmosphere similar to ZSM-5. Furthermore, Cu-SAPO-34 shows superior heat resistance even under wet atmosphere.

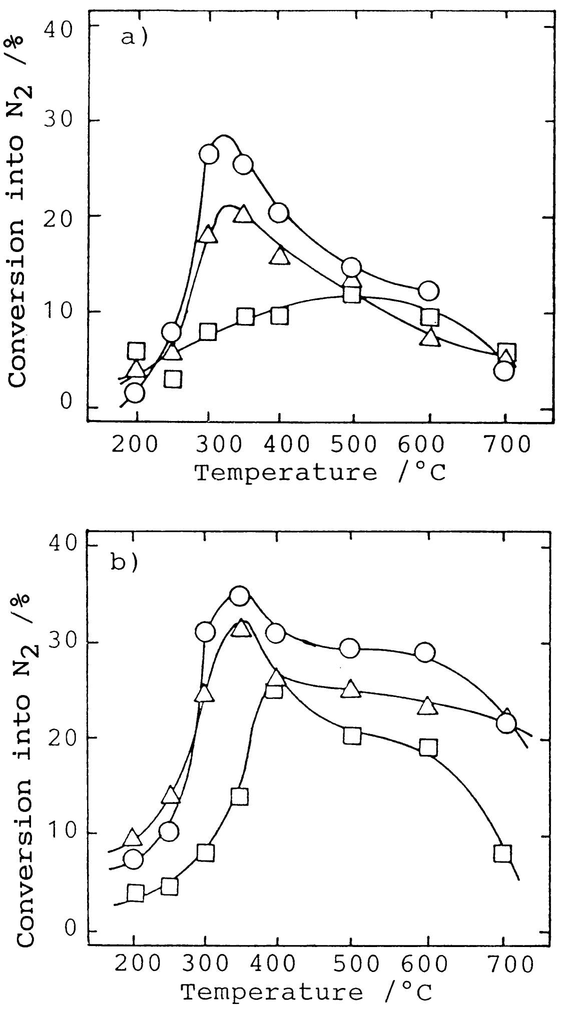

Fig. 4. Effect of heat treatment under atmosphere containing 3 vol.% of H_2O on the activity over (a) Cu-SAPO-34 and (b) Cu-ZSM-5 for NO reduction. (Precalcination at ○500 °C, △700 °C, □800 °C.)

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