Influence of SiO_2/Al_2O_3 molar ratio on adsorption of NO and NO_2 over Cu-mordenites and H-mordenites

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Introduction

Cu-mordenites catalysts are among the most active catalysts available for *de*-NOx at moderate temperatures. Silica-alumina molar ratio of mordenite strongly affects conversion efficiency for NOx. Catalytic experiments showed that the reduction of NOx to N_2 by hydrocarbons reaches 95-98 % depending on the catalyst composition.

The target of the present paper is to study influence of mordenite composition (SiO_2/Al_2O_3 molar ratio) on NO adsorption over Cu-mordenites.

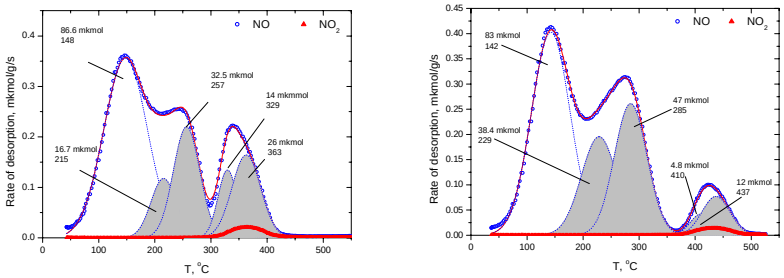
Materials and Methods

A series of protonated mordenites with variable SiO_2/Al_2O_3 molar ratio (MR) in the range $10 \leq MR \leq 206$ was supplied by TOSOH, Japan. Copper-containing samples were prepared by ion exchange in 0.1 N copper nitrate aqueous solution. The H-Mordenites and Cu-Mordenites as fine powders were used. Before the adsorption experiment, sample was pre-treated either in pure helium or in oxygen (25 vol%) in helium flow at temperature increase from ambient temperature to 520°C with rate 5°C/min and stored at 520°C for 1 h. The temperature was then decreased to 25°C, and after that a flow of He was purged trough sample followed by an adsorption from a flow of NO (1000 ppm) in helium. After equilibrium was achieved sample was purged with He to remove NO from gas phase and that physically adsorbed. Complicity of sample saturation with NO at adsorption and NO removal at sample purging was controlled by continuous NO analysis. TPD profiles of NO and NO_2 desorbed at linear heating of sample from 25 °C to 520 °C with a heating rate of 20°C/min were recorded continuously by NO-NO_2 gas analyzer "AO2020" (ABB-Hurtmann&Braun).

Results and Discussion

Si/Al molar ratio influences significantly both on number of peaks in TPD profiles and total quantity of NO/NO_2 desorbed (see example for CuMor with MR=15 in the Fig. 1). Introduction of copper leads to appearance of new peaks which could be assigned to NO adsorption over copper ions. Some conclusions were made concerning the nature of adspices formed by analysis of changes in contribution of different peaks with sample pretreatment. So, temperature maxima of peaks corresponding to NO adsorbed on Cu ions and their intensities are in strong dependence of oxidative/reductive sample pretreatment. Even so soft reduction of samples by heating in He flow changes significantly peak position in temperature scale. Quantity of NO desorbed for copper including samples with different Si/Al molar ratio (Fig.2) is in good agreement with catalyst activity in NO reduction by propane obviously indicating key role of Si/Al molar ratio in stabilization of definite copper centers effective in NO activation. The material of this work is of interest for understanding of copper behavior in zeolites and catalysts on their basis allowing to propose MR as the efficient tool in regulation of metal state that is important factor for catalytic activity and selectivity.

Figure 1. TPD profiles of NO and NO_2 for Cu-Mordenite 15 oxidized (left) and reduced (right).



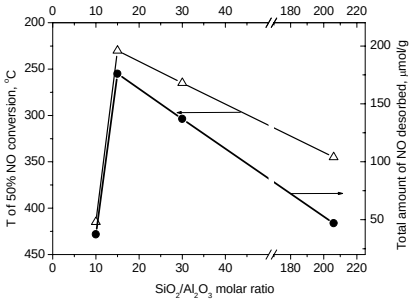


Figure 2. Catalytic activity in terms of temperature required for 50% NO conversion and total amount of NO desorbed in TPD profiles in dependence on Si/Al molar ratio in Cu-mordenites studied.

Significance

Quantity of NO desorbed for copper including samples with different Si/Al molar ratio is in good agreement with catalyst activity in NO reduction by propane obviously indicating key role of Si/Al molar ratio in stabilization of definite copper centers effective in NO activation.

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