A study of titanosilicates with MFI structure for SCR DeNO$_x$

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Introduction

Isomorphous substitution of Al^{+3} and/or Si^{+4} by transition metal ions such as Ti^{+4}, V^{+5}, and Fe^{+3} has attracted much attention because the second metal ions incorporated into zeolites could tune the catalytic properties [1-2]. Therefore, several interesting and useful catalysts could be prepared by putting two metal ions simultaneously into a zeolite framework [3-4]. According to the present study, we found the TS-1 zeolite having a MFI structure showed without a significant activity on the SCR activity of NO with NH_3. Therefore, in this study we intend to investigate how to tune up the SCR DeNOx activity of TS-1 zeolites either by impregnating a metal ion on the synthesized zeolites or via second metal ion incorporation into the framework TS-1.

Materials and Methods

The used zeolites were synthesized by the hydrothermal method and carried out using 450-ml capacity stainless-steel autoclaves under static conditions. A prepared crystalline bimetallosilicates is denoted as [M_{xx},Ti_{yy}]Z5, M=Fe, Co, and V; xx=Si/M; yy=Si/Ti). The SCR DeNO$_x$ reactions were performed in a fixed bed glass reactor under a down stream flow. Feed and product analyses were a combination of an on-line NO$_x$ analyzer (Echo Physics, CLD-700EL) with a dual channel chemiluminescent detector enabling a simultaneous determination of NO and NO_2 concentrations to calculate the NO conversion and an on-line gas chromatography equipped with a TCD detector and a 3 m x 1/8 in molecular sieve 5A column to quantify N_2 concentration.

Results and Discussion

The pure TS-1 zeolites showed no SCR DeNO$_x$ activity instead of catalyzing an oxidation of NH_3 into NO while the temperature was higher than 450 ^oC, This occurrence obviously results from the TS-1 zeolite having a redox property to carry on this catalytic reaction. Interestingly, the SCR DeNO$_x$ activity can be effectively tuned up when the metal oxides such as V_2O_5, CuO, Fe_2O_3, were impregnated onto the TS-1 zeolite, especially for V_2O_5. The activity of 5% V_2O_5/TS-l-20 catalyst is comparable to that of 5% V_2O_5/TiO_2. The SCR DeNO$_x$, activity of the V_2O_5/TS-1 catalyst showed the V_2O_5 loadings dependent. The activity increased with the V_2O_5 loadings till the weight percentage was twelve. Meanwhile the NO conversion to N_2 reached as high as 90% at 300 ^oC.

TS-1 with a second incorporated metal ion shows the DeNOx activity. [Fe40,Ti40]Z5 zeolite especially has a very high DeNO$_x$ activity within 380-500 ^oC. The NO conversion to N_2 reaches as high as 75%. Obviously, the properties of TS-1 zeolite are significantly modified by the incorporation of a second metal, Fe^{+3}, into the framework of zeolite. The SCR DeNO$_x$ activity is, therefore, strongly enhanced. Next, ratios of Fe/Si and Ti/Si also play an important role for the SCR DeNO$_x$ activity of [Fe,Ti]Z5 zeolite, as shown in Figure 1. The activity is further improved as the iron content increases. This may suggest that the iron ions in the framework are the active centers. For a further look insight this point, a comparison of the catalytic activity between 5% Fe_2O_3/TS-l-33 and [Fe,Ti]Z5 zeolite is made, the latter zeolite is much better the previous zeolites. It is evident that the framework iron ions (with a well-dispersed atomic state) possess a better catalytic activity than that of the iron oxide particles. This occurrence was also found in the previous study on the zeolite with MEL structure [3].

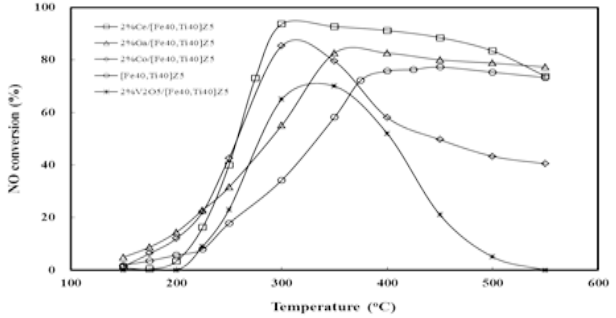

Figure 1. Effect of the impregnated metal ions on the SCR DeNO$_x$ activity of [Fe40,Ti40]Z5 zeolites.

Significance

Bimetallosilicates with MFI structure can be successfully synthesized by hydrothermal method. The incorporated second metal ions i.e., Fe^{+3}, or Co^{+3} or V^{+5}, can effectively modify and tune up the catalytic activity of TS-1 zeolite. Further, the SCR DeNO$_x$ activity can be very effectively enhanced through impregnating the metal oxides onto TS-1 or bimetallosilicates. CeO_2/[Fe,Ti]Z5 is the most active catalyst among the present synthesized zeolites and show a potential for applications.

References

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