Roles of Cu species and Brønsted acid sites in NH_3-SCR reactions over Cu/SAPO-34 catalysts

Lei Wang[1], Wei Li[2,*], Gongshin Qi[2], Steven J. Schmieg[2], Duan Weng[1]
[1] *School of Materials Science and Engineering, Tsinghua University, Beijing, P.R.China*
[2] *Chemical & Materials Systems Laboratory, General Motors Global R&D, Warren, MI, USA*
**wei.1.li@gm.com*

Introduction

Selective catalytic reduction of NO_x by ammonia (NH_3-SCR) has been extensively studied for lean NO_x control due to its high efficiency. Recently copper-based small-pore molecular sieves have been reported for NH_3-SCR with much improved activities and high thermal stability [1, 2]. The nature and location of the Cu species is critical for NH_3-SCR reaction [3]. Additionally, Brønsted acid sites in SAPO-34 molecular sieves also play an important role in both metal ion exchange process and reaction catalysis [4, 5]. In order to understand the roles of active species and Brønsted acid sites in NH_3-SCR reaction, Cu/SAPO-34 catalysts were systematically studied in this work by varying Cu species or Brønsted acidity, respectively.

Materials and Methods

Cu/SAPO-34 catalysts were synthesized via different methods in order to prepare samples with predominately single Cu species. Their activities for NH_3-SCR were evaluated under standard SCR conditions at various temperatures. The structure and nature of copper species were characterized in details by means of a variety of measurements (XRD, H_2-TPR, UV-*vis*, XAS, etc.). Brønsted acid sites were quantitatively estimated by using a combination of *in situ* DRIFTS and NH_3-TPD measurements. The types of surface adsorbed species and their reactivities in the NH_3-SCR reactions were studied by *in situ* DRIFTS and transient experiments.

Results and Discussion

In order to shed light on the active site requirements, Cu/SAPO-34 catalysts with different copper species were synthesized via ion-exchange and deposition precipitation methods, respectively. It was found that the isolated Cu ions at the exchange sites are the most active sites and they show outstanding catalytic performance and hydrothermal stability. Cu exchange enhances the NH_3 adsorption ability by introducing more Lewis acid sites while reduces the Brønsted acidity of SAPO-34. Hydrothermal treatment could promote the Cu species stabilized as isolated ions at the exchange sites within SAPO-34. Additionally, the Cu species from CuO clusters on the external surface migrate to the ion-exchanged sites inside the micropores of SAPO-34 during the hydrothermal treatment and the migration mechanism was studied by *in situ* XAS measurements.

In addition, a series of Cu/SAPO-34 catalysts with different Brønsted acidities were synthesized by titrating the Brønsted acid sites with potassium ions to understand the NH_3-SCR activity-acidity correlations. Potassium was found to have little effect on the Cu species at the ion exchange sites and the copper loadings remained unchanged. The number of Brønsted acid sites was quantitatively estimated by using a combination of *in situ* DRIFTS and NH_3-TPD measurements. A linear relationship was found between the number of Brønsted OH groups determined by DRIFTS and the amount of NH_3 desorbed at high temperatures from NH_3-TPD. NH_3 species adsorbed on Brønsted acid sites show a higher thermal stability. With the same copper loading, the stronger Brønsted acidity leads to higher NO conversion and hydrothermal stability. The Brønsted acid sites are required for the NH_3-SCR reaction at high temperatures to provide more active ammonia species.

Cu/SAPO-34 catalysts exhibit superior adsorption ability of NH_3 rather than NO and the NH_3 species adsorbed on Cu sites are more reactive than those on Bronsted acid sites. On the basis of these results, the mechanism for NH_3-SCR reaction is proposed as shown in Fig. 1: 1) At low temperatures, the ammonia adsorbed on the Cu^{n+} sites is stable and NH_3-SCR reaction rate is limited by the surface reaction rates; 2) At high temperatures, the reaction rate is limited by NH_3 migration from the Brønsted acid sites to the Cu^{n+} sites due to a decreasing NH_3 coverage.

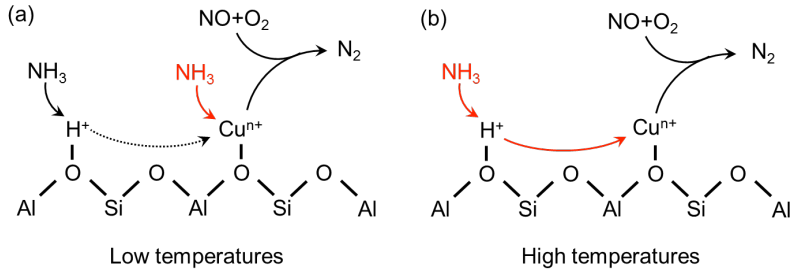

Figure 1. Proposed mechanism for NH_3-SCR reaction over Cu/SAPO-34.

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