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Review

Recent advances in the selective catalytic reduction of NOx with NH_3 on Cu-Chabazite catalysts

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ABSTRACT

The development of Cu-chabazite (CHA) catalysts, i.e. Cu-SSZ-13 and Cu-SAPO-34, represents a significant technology breakthrough for the removal of NOx by selective catalytic reduction (SCR) with ammonia. Cu-CHA catalysts show an excellent hydrothermal stability towards high temperature aging and wide active temperature windows for the ammonia SCR reaction. This work summarizes the recent progress in the development of the Cu-CHA catalysts for the NH_3-SCR reaction. The state of Cu in the reaction and the preparation methods on the catalytic performance are discussed. The advances in the understanding of the reaction mechanism are reviewed. The hydrothermal stability of the typical Cu-CHA catalysts are compared.

Contents

1. Introduction

Nitrogen oxides (NOx), in the flue gas of industrial combustion and vehicle exhaust, are among the major air pollutants that lead to a number of environmental problems such as photochemical smog, acid rain and haze. To meet the stringent emission standards, many approaches, such as three-way catalysis [1], NOx storage and reduction (NSR) and selective catalytic reduction (SCR) of NOx with ammonia, to reduce the NOx emissions have been intensively explored. Among these techniques, the SCR of NOx with NH_3 is considered to be the most efficient technology for reducing NOx emission in the presence of excess oxygen [2]. V_2O_5-$WO_3(MoO_3)/TiO_2$ material has been commercially employed as a NH_3-SCR catalyst for a number of years. However, several serious problems with this catalyst still remain, e.g. the narrow temperature window, i.e. only applicable in 300–400 °C, the high activity of SO_2 oxidation, and the toxicity of V_2O_5 [3]. Therefore, new catalysts with environmentally benign characteristics and high SCR performance in a wide temperature range are required. Since the

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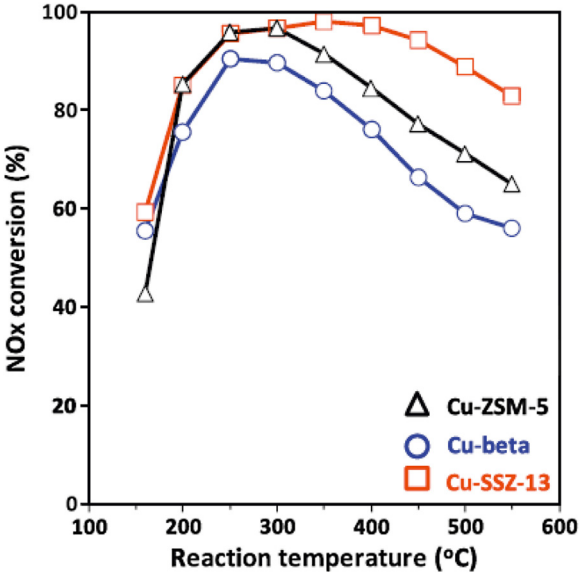

Fig. 1. NOx conversion profiles for Cu-SSZ-13, Cu-beta and Cu-ZSM-5 at various temperatures. Reaction conditions: 350 ppm NO, 350 ppm NH_3, 14% O_2 and 2% H_2O with a balance of N_2.
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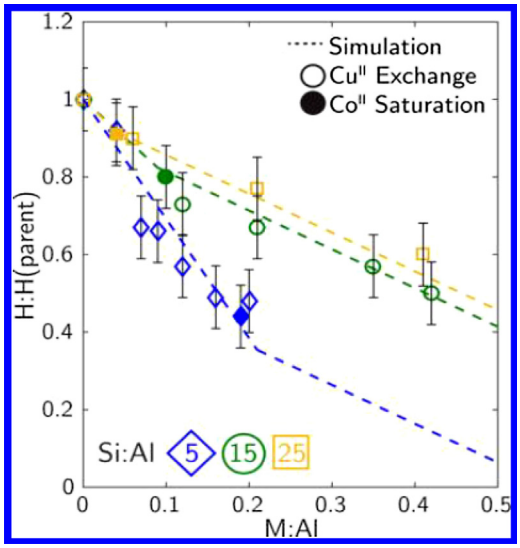

Fig. 2. Residual H+ sites per parent sample H+ from NH_3 titrations on oxidized M-SSZ-13 samples versus extent of M/Al exchange for Si:Al = 5 (blue ◊), 15 (green ○), and 25 (orange □). Open and filled symbols denote Cu^{2+} and saturated Co^{2+} exchange, respectively. Dashed lines are model predictions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).
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discovery of Cu-ZSM-5 catalyst as an efficient catalyst for NOx removal in 1986 by Iwamoto *et al.* [4], Cu-exchanged zeolites such as ZSM-5, BEA and Y have been investigated [5]. However, the poor hydrothermal stability of Cu-exchanged of those zeolite catalysts significantly limits their application in the treatment of exhaust gas from diesel engine [5].

Recently, Cu-SAPO-34 [6] and Cu-SSZ-13 [7] (Chabazite structured) catalysts with very high hydrothermal stability and activity for the NH_3-SCR reaction under oxidizing conditions were discovered by the industrial researchers. Kwak et al. [8] first reported the performance of Cu-SSZ-13 in NH_3-SCR reaction, with comparison to the data of Cu-BEA and Cu-ZSM-5 zeolites. The order of the catalyst performance observed was Cu-SSZ–13 > Cu-ZSM–5 > Cu-Beta (see Fig. 1), that is the inverse order of the pore size. SAPO-34 and SSZ-13 are typical examples of zeolites with the CHA structure, that have small pore radius of eight-membered rings (3.8 Å). Both Cu-SSZ-13 and Cu-SAPO-34 samples are reported to maintain their high SCR performance even after hydrothermal aging at 800 °C [9]. Although SAPO-34 and SSZ-13 share the same CHA structure, Cu-SAPO-34 is more complicated than Cu-SSZ-13 [10–13]. Unlike SSZ-13, in which Brønsted acid sites are highly dependent on the content of Al, the Brønsted acid sites of SAPO-34 are attributed to the introduction of Si atoms into the neutral $AlPO_4$-34 framework [14]. It was proposed that Si atoms incorporate into the AlPO4-34 structure by two different substitution mechanisms: the first one (denoted as SM1) is that the Si substitution for phosphorus form Si(4Al) entities, which give rise to negative charges for forming Brønsted acid sites; the second mechanism (denoted as SM2) is the double substitution of neighboring aluminum and phosphorus by two silicon atoms to form Si(nAl) (n = 3–0) structures, which leads to the formation of stronger Brønsted acid sites [12,14]. However, a large amount of Si islands are formed when Si content is high, which has no acid site. Many factors including the template, the Al and Si source, the molar ratio of Si/Al/P/template of the gel, the reaction temperature and reaction time influence the dispersion of Si in the SAPO-34 [14–16]. This makes it difficult to determine the acid density and acid strength of SAPO-34.

Recently, the advances in the removal of NOx by NH_3-SCR reaction over CHA-based catalysts are reviewed by Beale *et al.* [17] and Moliner *et al.* [18]. They mainly discussed the key findings of the synthesis method and characterization work over CHA-structured based zeolite catalysts. In this work, we pay attention to the state of Cu in the reaction over Cu-CHA catalysts. The reaction mechanism, and the comparison between Cu-SSZ-13 and Cu-SAPO-34 catalysts as well as the future prospects, are outlined.

2. State of Cu in the catalyst

The performance of the Cu-CHA catalyst strongly depends on the chemical state of Cu during the reaction. It is now accepted that the isolated Cu^{2+} is the active sites in Cu-CHA catalyst for NH_3-SCR reaction [19–21]. Gao *et al.* [22] investigated the influence of the ion-exchange level on the Cu species in Cu-SSZ-13 catalyst. They found that the catalysts with low-exchange level contain exclusively isolated Cu^{2+} at the 6-membered ring sites containing two framework Al atoms. Due to the high SCR activity of the samples, the isolated Cu^{2+} at the 6-membered ring sites of SSZ-13 is believed to be the active site for the SCR reaction. However, with the further increase of the ion-exchange level, a Cu_xO_y species (clustered Cu^{2+} ions, $y \geq 1$) forms and locates at the 8-membered ring. This species also is found to be active for ammonia oxidation. Verma et al. [23] also evaluated the Cu species in Cu-SSZ-13 catalysts with Si/Al atomic ratio of 4.5 and found that there is a theoretical limit for the density (Cu:Al atomic ratio = 0.2) of the isolated Cu^{2+} at the 6-membered rings in SSZ-13. Beyond this limit, a part of the isolated Cu^{2+} ions convert to Cu dimers. Based on the operando characterization and density functional theory (DFT) calculations [19,20], the isolated Cu^{2+} at the 6-membered ring sites of SSZ-13 was confirmed to be the active site for the NH_3-SCR reaction under realistic conditions at low temperatures. The NH_3-SCR reaction was proposed to be associated with a closed redox cycle between Cu^{2+} and Cu^{+}/H^{+} formed at the 6-membered rings containing two framework Al atoms [20].

The isolated Cu^{2+} was found to firstly occupy the site in 6-membered ring with 2 Al atoms after dehydration [24–26], when the similar sites saturate, the Cu species may exist with an OH extra-ligand coordinate to the 1 Al sites. Paolucci et al. [27] confirmed this result by the experiments and DFT simulation. As shown in Fig. 2, at