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Experimental and kinetic modeling study of NH_3-SCR of NO*x* on Fe-ZSM-5, Cu-chabazite and combined Fe- and Cu-zeolite monolithic catalysts

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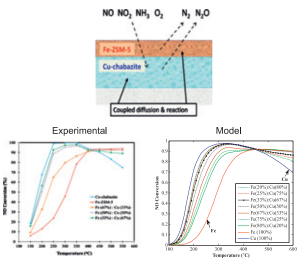
HIGHLIGHTS

- ▸ First experimental and kinetic modeling study of Cu-chabazite SCR catalyst.
- ▸ 1+1 dimensional monolith model combines multi-reaction global kinetics and mass transport.
- ▸ Model predicts conversion and selectivity trends for standard, fast, and NO_2 SCR.
- ▸ Model confirms expanded high NO*x* conversion temperature window for combined Fe/Cu catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

A comprehensive experimental and modeling study of selective catalytic reduction of NO*x* with NH_3 was carried out on Fe-ZSM-5 and Cu-chabazite (CHA) catalysts. The experiments reveal that Cu-CHA catalyst has a higher NH_3 storage capacity and activity for NH_3 oxidation and standard SCR compared to Fe-ZSM-5. The NO*x* reduction activity on the Fe-ZSM-5 catalyst was found to be strongly dependent on the NO_2 feed fraction in contrast to Cu-CHA catalyst for which NO*x* conversion was much less sensitive to NO_2. In the presence of excess NO_2, both N_2O and ammonium nitrate were produced on both catalysts although Fe-ZSM-5 catalyst had a higher selectivity towards these byproducts compared to Cu-CHA. For different feed conditions ($NO_2/NOx=0$–1), Cu-CHA was a more active NO*x* reduction catalyst at lower temperatures (<350 °C) while Fe-ZSM-5 was more active at higher temperatures (>400 °C). Global kinetic models were developed to predict the main features of several SCR system reactions investigated experimentally. The models account for NH_3 adsorption, NH_3 oxidation, NO oxidation, standard SCR, fast SCR, NO_2 SCR, ammonium nitrate formation and its decomposition to N_2O, N_2O decomposition and N_2O reduction by NH_3. The 1+1 dimensional reactor model accounts for potential washcoat diffusion limitations. The model accurately predicts the steady state NO*x* and NH_3 conversions and the selectivity of the different products formed during these reactions. The model was used to predict the performance of standard and fast SCR reactions on combined systems of Fe- and Cu-zeolite monolithic catalysts which were found to have higher NO*x* conversion activity over a wider temperature range than with individual Fe- and Cu-zeolite catalysts as reported in our earlier study (Metkar et al., 2012b). Among various configurations of the combined catalysts, either a single brick made up of a dual-layer catalyst with a thin Fe-zeolite layer on top of a thick Cu-zeolite layer or a sequential arrangement of short Fe-ZSM-5 brick followed by longer Cu-CHA brick resulted in high NO*x* removal efficiency over a wide temperature range of practical interest.

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1. Introduction

Selective catalytic reduction (SCR) of NO*x* with NH_3 is considered as the most promising technology to meet the stringent EPA standards of NO*x* emissions for heavy duty vehicles. The SCR of NO*x* with NH_3 has been studied extensively on various catalysts including vanadia–titania catalysts (Ciardelli et al., 2004, 2007; Koebel et al., 2001), Cu-zeolites (Colombo et al., 2010; Komatsu et al., 1994; Sjovall et al., 2006) and Fe-zeolites (Coq et al., 2000; Grossale et al., 2008a, 2008b; Metkar et al., 2011b).

The standard SCR reaction between NO and NH_3 occurs in the presence of oxygen:

$$4NH_3+4NO+O_2\rightarrow 4N_2+6H_2O. \tag{1}$$

Many studies have shown that the NO*x* reduction activity increases if NO and NO_2 are fed in equimolecular amount (Colombo et al., 2010; Devadas et al., 2006). The reaction between equimolar amounts of NO and NO_2 with NH_3 is known as the fast SCR reaction:

$$2NH_3+NO+NO_2\rightarrow 2N_2+3H_2O. \tag{2}$$

The third important reaction in this chemistry is NO_2 SCR reaction:

$$4NH_3+3NO_2\rightarrow 3.5N_2+6H_2O. \tag{3}$$

This reaction is important when the feed NO*x* comprises mostly NO_2. While the presence of NO_2 accelerates the NO*x* reduction rate on various catalysts (Colombo et al., 2010), its presence complicates the overall NH_3-SCR reaction chemistry (Schwidder et al., 2008). NO_2 has been proposed as the key species for the SCR of NO*x* with NH_3 on various zeolite catalysts, and the oxidation of NO to NO_2 is the likely rate-limiting step (Kiovsky et al., 1980). Stevenson et al. (2000) and Wallin et al. (2003) argued that oxidation of NO is the rate determining step in the reduction of NO by NH_3 on H-ZSM-5. The oxidation of NO to NO_2 has been proposed to be the rate limiting step for the standard SCR reaction on Fe-zeolite catalysts (Devadas et al., 2006; Huang et al., 2002; Metkar et al., 2011b). Many other studies have focused on the mechanistic issues for the SCR chemistry. Komatsu et al. (1994) suggested a mechanism for the standard SCR reaction on Cu-zeolite catalysts that involves the formation of a bridging NO_3 molecule which further reacts with NO to form NO_2. The NO_2 then reacts with NH_3 to produce N_2 and H_2O. Sun et al. (2001) presented a mechanistic model on Fe-MFI catalysts in which the preferred path for NO*x* reduction with ammonia occurs via ammonium nitrite which decomposes to N_2 and H_2O. Other studies have suggested that the reduction of NO and NO_2 by NH_3 involves the formation of HNO_2 and HNO_3 (Choi et al., 1996; Eng and Bartholomew, 1997; Richter et al., 1998; Yeom et al., 2005).

In spite of a host of experimental studies focused on mechanistic issues and reaction pathways, a much smaller number of studies have focused on the kinetic modeling of NH_3-SCR reactions. Several studies presented steady-state global kinetic models for the standard SCR for vanadia-based catalysts (Dumesic et al., 1996; Roduit et al., 1998; Willi et al., 1996), Cu-ZSM-5 (Baik et al., 2006; Olsson et al., 2008) and Cu-faujasite (Delahay et al., 2004). Nova et al. developed a detailed transient kinetic model for the SCR reaction system on vanadia-based catalyst (Nova et al., 2006, 2009) while Chatterjee et al. (2006, 2007, 2010) developed a global kinetic model for both vanadia- and Fe-zeolite catalysts. Their model describes well the transient and steady-state NO*x* conversion and the effect of feed NO/NO_2 ratio on the NH_3-SCR chemistry. Olsson and co-workers developed both global and detailed kinetic models for NH_3-SCR reactions on Fe-ZSM-5 and Cu-ZSM-5 catalysts (Olsson et al., 2008, 2009; Sjovall et al., 2009a, 2009b, 2010). Their kinetic models account for transient effects for various feed concentrations of NO_2. Finally, some other studies present kinetic models predicting transient behaviors of NH_3-SCR reactions on Fe-zeolite catalysts (Colombo et al., 2012; Malmberg et al., 2007; Sjovall et al., 2010).

The main objective of the current study is to develop a global kinetic model that predicts the main features of various reactions occurring during NH_3-SCR on both Fe-ZSM-5 and Cu-chabazite (CHA) catalysts. In spite of the above mentioned progress in the kinetic modeling of NH_3-SCR, including the availability of kinetic models for various Fe- and Cu-exchanged zeolites, to our knowledge there is no kinetic model available for the recently commercialized small pore Cu-CHA catalyst. [Remark: Cu-CHA has emerged as the NH_3-SCR catalyst of choice because of its combination of high activity, and hydrothermal stability.] Moreover, the aforementioned models do not account for potential external transport or washcoat diffusion limitations. Our recent study determined the extent of washcoat diffusion limitations in Fe- and Cu-zeolite catalysts for NH_3-SCR reactions (Metkar et al., 2011a). Such limitations were found to be important for each of the SCR reactions and should be included in any SCR reactor model. For example, for the standard SCR on Fe-ZSM-5, diffusion limitations are important for temperatures above ca. 300 °C; for fast SCR the threshold temperature is closer to 200 °C (Metkar et al., 2011a). To this end, not including washcoat diffusion prevents consideration of more complex multi-layer catalysts for which diffusion and reaction coupling is integral to the overall performance; examples include the multi-metal exchanged zeolite catalyst in the current study, dual-layer ammonia slip catalysts, and dual-layer LNT/SCR catalysts, among others.

In the current study, we present a $1+1$ dimensional reactor model, which includes external transport and washcoat diffusion processes, for both the Fe-ZSM-5 and Cu-CHA catalysts. The kinetic model considers ammonia adsorption and desorption, NH_3 oxidation, NO oxidation, standard SCR, fast SCR, NO_2 SCR, ammonium nitrate formation, N_2O formation, N_2O decomposition and N_2O SCR reactions. In addition to predicting the performance of NH_3-SCR on Fe-ZSM-5 and Cu-CHA catalysts, the model is used to simulate combined Fe- and Cu-zeolite catalysts, including sequential brick and dual-layer configurations. In a recent study (Metkar et al., 2012b), we showed how the catalyst performance in terms of the high temperature performance window can be improved through the judicious combinations of Fe- and Cu-exchanged zeolites. We use the model to predict these improvements and go further to estimate compositions and architectures that provide improved performance.

2. Experimental

2.1. Catalyst samples

The commercial Cu-zeolite catalyst was supplied by BASF (Iselin, NJ). It is a small-pore Cu-chabazite (CHA) type catalyst, established in patents and communicated in recent papers to possess excellent hydrothermal stability (Bull et al., 2009; Fickel et al., 2011; Kwak et al., 2010). The Cu loading was about 2.5%. The commercial washcoated Fe-zeolite (ZSM-5 type) catalyst was supplied by an unnamed catalyst manufacturer. The sample had a Fe loading of about 3 wt% in the monolith washcoat. Both commercial samples had a cell density of 400 cpsi and effective (peripheral-averaged) washcoat thickness of about 45–50 μm.

Dual-layer catalysts were prepared by depositing Fe- and Cu-ZSM-5 catalysts on the commercial catalysts. We used a dip-coating technique to synthesize these dual-layer catalysts. This procedure has been described in detail elsewhere (Metkar et al., 2011a, 2011b, 2012a, 2012b). The Cu-ZSM-5 layer was deposited on the commercial Fe-ZSM-5 catalyst by dipping the