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A kinetic model for ammonia selective catalytic reduction over Cu-ZSM-5

Louise Olsson [a,*], Hanna Sjövall [a], Richard J. Blint [b]

[a] *Competence Centre for Catalysis, Chemical Reaction Engineering, Chalmers University of Technology, 412 96 Göteborg, Sweden*
[b] *General Motors R&D Center, Chemical and Environmental Sciences Laboratory, 30500 Mound Road, Warren, MI 48090-9055, United States*

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Abstract

Kinetic modeling, in combination with flow reactor experiments, was used in this study for simulating NH_3 selective catalytic reduction (SCR) of NO_x over Cu-ZSM-5. First the mass-transfer in the wash-coat was examined experimentally, by using two monoliths: one with 11 wt.% wash-coat and the other sample with 23 wt.% wash-coat. When the ratio between the total flow rate and the wash-coat amount was kept constant similar results for NO_x conversion and NH_3 slip were obtained, indicating no significant mass-transfer limitations in the wash-coat layer. A broad range of experimental conditions was used when developing the model: ammonia temperature programmed desorption (TPD), NH_3 oxidation, NO oxidation, and NH_3 SCR experiments with different NO-to-NO_2 ratios. 5% water was used in all experiments, since water affects the amount of ammonia stored and also the activity of the catalyst. The kinetic model contains seven reaction steps including these for: ammonia adsorption and desorption, NH_3 oxidation, NO oxidation, standard SCR ($NO + O_2 + NH_3$), rapid SCR ($NO + NO_2 + NH_3$), NO_2 SCR ($NO_2 + NH_3$) and N_2O formation. The model describes all experiments well. The kinetic parameters and 95% linearized confidence regions are given in the paper. The model was validated with six experiments not included in the kinetic parameter estimation. The ammonia concentration was varied from 200 up to 800 ppm using NO only as a NO_x source in the first experiment and 50% NO and 50% NO_2 in the second experiment. The model was also validated with transient experiments at 175 and 350 °C where the NO and NH_3 concentrations were varied stepwise with a duration of 2 min for each step. In addition, two short transient experiments were simulated where the NO_2 and NO levels as well as NO_2-to-NO_x ratio were varied. The model could describe all validation experiments very well.
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1. Introduction

Diesel engines and lean burn gasoline engines have better fuel economy compared to stoichiometric gasoline engines. However, the conventional three-way catalyst (TWC) cannot reduce the NO_x efficiently, due to the high oxygen content in the exhaust. It is important to decrease the emissions of NO_x for environmental reasons [1,2].

There are three major techniques for reducing NO_x in lean atmosphere; lean NO_x traps [3,4], selective catalytic reduction using hydrocarbons (HC SCR) [1,5,6] and urea selective catalytic reduction (urea SCR) [7–40]. The focus of this work is NH_3 SCR. The ammonia is produced by the decomposition of urea (NH_2–CO–NH_2) [7,8], which can be summarized by the following reactions:

$$NH_2-CO-NH \rightarrow NH_3 + HNCO \quad (1)$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \quad (2)$$

There are many experimental studies on ammonia/urea SCR over different catalysts [9–27], where vanadia is the most well studied catalyst [9–15]. Zeolites are also extensively studied for this reaction; examples of zeolites that have been experimentally investigated for NH_3 SCR are Cu-ZSM-5 [16–20], Cu-faujasite [21,22], H-ZSM-5 [23,24] Fe-ZSM-5 [25,26] and Fe-zeolite-beta [27]. Rahkamaa-Tolonen et al. [19] investigated

* Corresponding author. Tel.: +46 31 772 4390; fax: +46 31 772 3035.
E-mail address: louise.olsson@chalmers.se (L. Olsson).

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Nomenclature

a_j	active site density for reaction j (mol-sites/m^3)
A	pre-exponential factor. Depends on rate expression. (The concentrations in the rates are in mol/m^3 and the rates in unit s^{-1})
A_{tot}	front area of the monolith (m^2)
$c_{g,tot}$	the total concentration in the gas bulk, where the temperature is T_g (mol/m^3)
$c_{s,i}$	the molar concentration of the gas specie i at the catalyst surface (mol/m^3)
$c_{s,tot}$	the total concentration at the catalyst surface, where the temperature is T_s (mol/m^3)
D_h	hydraulic diameter of channel (m)
$D_{i,m}$	binary diffusion coefficient of specie i in the mixture (m^2/s)
E_a	activation energy (J/mol)
k	rate constant. Depends on rate expression. (The concentrations in the rates are in mol/m^3 and the rates in unit s^{-1})
$k_{m,i}$	mass-transfer coefficient for specie i (mol/m^2 s)
nr	number of reactions
P_{tot}	total pressure (Pa)
r_j	reaction rate for reaction j (mol/mol-sites s)
R	gas constant (J/mol K)
Sh	Sherwood number
s_{ij}	stoichiometric coefficient of specie i in reaction j
s_{kj}	stoichiometric coefficient of surface specie k in reaction j
S	surface area per reactor volume (m^{-1})
t	time (s)
T_s	temperature at catalyst surface (K)
w	molar flow rate (mol/s)
$x_{g,i}$	mole fraction of gas specie i
$x_{s,i}$	mole fraction of gas specie i at the surface
z	axial position (m)

Greek symbols

α	constant
θ_k	coverage of component k

several zeolites: hydrogen, copper, iron and silver ion-exchanged ZSM-5, mordenite, beta, ferrierite and Y-zeolites.

There are three SCR reactions described in the literature depending on the NO_x source, the standard SCR using NO, the rapid SCR with NO and NO_2 and NO_2 SCR with NO_2 only:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (3)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (4)$$

$$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O \quad (5)$$

It is observed that about 50% of NO_2 is optimum concentration and this has been seen on several catalysts, including vanadia [28], Cu-ZSM-5 [16] and Fe-ZSM-5 [25]. The "Rapid SCR" reaction describes this property well. Tronconi et al. [15] and Chatterjee et al. [29], have suggested a detailed mechanism of this step on vanadia catalysts. Further, at lower temperatures (<200 °C), the ammonia can react with NO_2 producing ammonium nitrate (NH_4NO_3), which may deposit on the catalyst [30], leading to temporary deactivation. NH_4NO_3 is decomposed, primarily to HNO_3 and NH_3 at higher temperature [28]. The formation of ammonium nitrate on vanadia-based catalysts was studied in detail by Ciardelli et al. [14].

Kinetic modeling has been performed for NH_3 SCR. Global models for the standard SCR ($NH_3 + NO + O_2$) under steady-state conditions are presented for vanadia-based catalysts [10,12,31], Cu-ZSM-5 [20], Cu-faujasite [21], HZSM-5 [23] and chromia on titania [32]. However, there are very few kinetic models that consider the effects of transients and the NO-to-NO_2 ratio. Winkler et al. [33] presented a transient model for SCR on a commercial vanadia/titania catalyst. The rates for the rapid and NO_2 SCR from this work were used by Wurzenberger and Wanker [34] in their model for SCR on vanadia. Further, Wurzenberger and Wanker [34] have multiple reaction rates for the standard NH_3 SCR and NH_3 oxidation (four rates for two reactions), where one reaction step is for the steady-state rate and the other one for transients. Lietti et al. [35] developed a transient kinetic model for the standard SCR reaction over vanadia. Chatterjee et al. [29] presents a global kinetic model, with high level of details, for vanadia-based catalysts. The model can adequately describe transients and steady-state conversion and the effect of NO/NO_2 ratio. Further, Malmberg et al. [39] presents a transient model for NH_3 SCR with NO over Fe-zeolite. In a recent study Chatterjee et al. [40] present a transient model over a commercial zeolite, which also includes the rapid SCR reaction.

There are no kinetic models and kinetic parameters published on ammonia SCR over Cu-zeolites, which consider transient experiments and NO-to-NO_2 ratio. The objective of this work is to develop a kinetic model for Cu-ZSM-5. The influence of NO-to-NO_2 ratio was investigated and all experiments contained 5% H_2O. The model considers ammonia adsorption and desorption, NH_3 oxidation, NO oxidation, standard SCR, rapid SCR, NO_2 SCR and N_2O formation. The model is validated with separate experiments not included in the fitting procedure where the ammonia concentration was varied and also four experiments containing short transients. The model can describe these validation experiments well.

2. Experimental

2.1. Catalyst preparation and characterization

All four monolith coated catalysts used in this study were prepared using H-ZSM-5 powder acquired from Alsi-Penta. Details about the ion-exchange and preparation can be found in Ref. [16]. The initial material was H-ZSM-5 with a SiO_2/Al_2O_3 ratio of 27. The zeolite was first ion-exchanged with sodium, using $NaNO_3$, in order to get a more controlled ion-exchange. This was followed by ion-exchange with copper ($Cu(CH_3COO)_2$). The cordierite monoliths had a cell density of 400 cpsi

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