A Kinetic Model for the Selective Catalytic Reduction of NO_x with NH_3 over a Fe-zeolite Catalyst

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Introduction

Emissions from the combustion of fossil fuel contain several pollutants which can be converted over a catalyst to less harmful products. An efficient way to reduce nitrogen oxides (NO_x) in a lean environment is to apply the selective catalytic reduction of these oxides with ammonia (NH_3 SCR). The mechanism that describes SCR of NO_x with ammonia is not fully understood and there are various reaction pathways and reaction intermediates proposed in the literature. In this study we develop a kinetic model for a commercial Fe-zeolite catalyst in order to improve the understanding of the actual catalytic reactions that takes place over this catalyst. The model accounts for ammonia storage, ammonia oxidation, NO oxidation, the SCR of NO and mixtures of NO and NO_2 including excess NO_2, ammonia inhibition and N_2O formation. The model describes the steady-state and transient catalytic activity in several feed mixtures at temperatures from 150ºC to 650ºC.

Materials and Methods

Flow reactor experiments were carried out over a commercial Fe-zeolite catalyst at a space velocity of about 25 000 h^{-1}. The catalyst used was a washcoated monolith with a cell density of 400 cpsi. The outlet gases were analyzed by a MultiGas™ 2030 FTIR instrument. All experiments were carried out in presence of O_2, H_2O and CO_2 at temperatures from 150ºC to 650ºC.

A kinetic model for the SCR of nitrogen oxides was developed, which accounts for effects such as: ammonia storage, NO and NH_3 oxidation, NH_3 SCR of mixtures of NO and NO_2, ammonium nitrate formation, ammonia inhibition and formation of N_2O. Two kinds of sites were included in the model, one type of site to accounts for the active Fe-sites, and a second kind to account for additional weakly bound ammonia. The model is based on a total of twelve summary reaction rates.

Results and Discussion

Steady-state results from NH_3 SCR experiments are shown in Figure 1. The feed consisted of 510 ppm NH_3, 510 ppm total NO_x, 8 % O_2, 5 % H_2O, and 5 % CO_2. The composition of total NO_x was varied using 0, 50 % or 75 % NO_2. and the temperature was increased stepwise from 150ºC to 650ºC. The conversion of NO is about 10 % at 150ºC and increases each time the temperature is raised if no NO_2 is fed. The NO_x reduction reaches 92 % at 500ºC but decreases again at higher temperature due to the rapid NH_3 oxidation that occurs at 650ºC. The SCR activity is high already at 150ºC and stays at about 95 % conversion up to

500ºC if about equal amounts of NO and NO_2 is fed to the reactor. However, if larger fraction of NO_2 is fed, the activity at low temperature drops. It is thus clear that the NO_x reduction activity increases if NO_2 is introduced to the feed, and that about equal amounts of NO and NO_2 is beneficial at temperatures up to 500ºC. However, at 650ºC, the highest conversion is observed if NO is used. The formation of N_2O is low up to equal amounts of NO and NO_2, but at the highest NO_2 fraction, formation of N_2O can not be neglected (not shown here). The model is able to describe the steady-state conversion of both NO_x and NH_3 well throughout all experiments. The model was developed to account for both steady-state and transient conditions, and was also validated using shorter transient experiments, additional ammonia storage experiments and experimental conditions not used in the parameter estimation and was able predict these new conditions adequately.
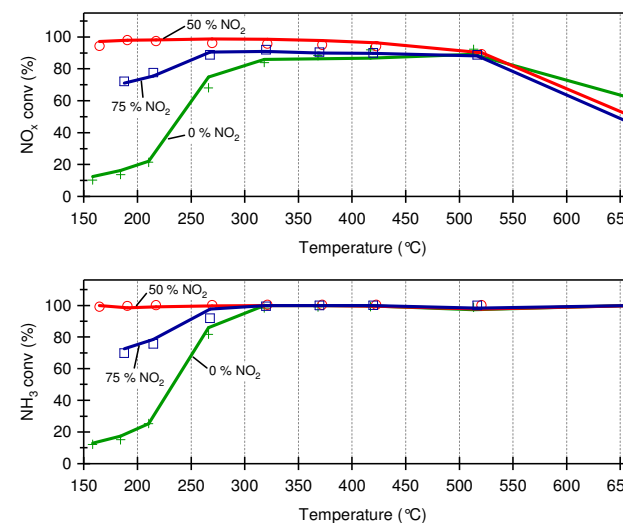

Figure 1. Experimental and calculated steady-state conversions of NH_3 and NO_x. The catalyst was exposed to 510 ppm NH_3, 510 ppm total NO_x, 8 % O_2, 5 % H_2O, 5 % CO_2. The composition of total NO_x was varied using 0, 50 % or 75 % NO_2. Markers show the experimental conversions and the solid lines show the calculated conversions.