Modeling of Cu/SSZ-13 SCR catalyst sulfation depending on HTA-induced changes in ZCuOH and Z_2Cu site distribution

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Significance and Relevance

Selective catalytic reduction (SCR) of nitrogen oxides (NOx) remains a key topic in environmental catalysis, and catalyst aging and sulfur poisoning are critical issues for practical application. The novel aspect of this work lies in developing a mathematical model that captures changes of ZCuOH and Z_2Cu site distribution during hydrothermal aging of Cu/SSZ-13 SCR catalyst and combines them with the SO_2 oxidation and sulfation kinetics specific to the individual Cu site types. The model offers a deeper understanding of the degradation mechanisms, which is crucial for predicting catalyst lifespan and optimizing SCR technology for reliable NO_x emissions control in real-world conditions.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Air cleaning and combustion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Selective catalytic reduction (SCR) with Cu/SSZ-13 catalysts is the leading approach for reducing nitrogen oxides (NOx) emissions from diesel engines. Within the catalyst, various active sites exist, including mono- and multinuclear framework copper sites and extra-framework CuO nanoparticles[1]. The literature primarily discusses two framework sites: ZCuOH and Z_2Cu. The main mechanisms of Cu/SSZ-13 catalyst deactivation are hydrothermal aging (HTA) and sulfur poisoning. Mild HTA, at temperatures below 750°C, preserves the zeolite structure but promotes the transformation of ZCuOH sites to Z_2Cu, affecting catalyst performance[2]. Recently we developed a kinetic model that describes transformation of the Cu sites during mild HTA and quantified different activity of ZCuOH and Z_2Cu sites in NO, CO, NH_3 and SO_2 oxidation reactions[3]. This work utilizes an integrated experimental and kinetic modeling approach to examine the effect of combined HTA and sulfur poisoning on the standard SCR reaction rate.

Materials and Methods

The Cu/SSZ-13 catalyst used in this study was provided by Cummins Inc. and was washcoated onto a cordierite monolith structure with a cell density of 600 cpsi. The SSZ-13 zeolite had a Si:Al ratio of 9.5, and the copper loading was 2.2 wt.%. All experiments were performed in a tubular flow lab reactor. In situ techniques, including diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), NH_3-TPD, H_2-TPR, and NH_3+NO titration, were utilized to quantify the active sites in the catalyst samples. The SCR reaction was investigated at steady-state over a temperature range of 150–500 °C, comparing the activity of the catalyst in four different states: (i) fresh catalyst, (ii) fresh catalyst sulfated at 400°C, (iii) hydrothermally aged catalyst, and (iv) hydrothermally aged catalyst sulfated at 400°C. Mild hydrothermal aging was performed at 650 °C for 5 hours. Both fresh and hydrothermally aged samples were sulfated in the presence of 30 ppm SO_2, 10% O_2, 7% H_2O, and balance N_2 at 400 °C. A heterogeneous 1D plug-flow model was used to simulate transport and reactions in the catalyst, incorporating mass and enthalpy balances for the gas and solid phases along the reactor. The kinetic equations include NH_3 adsorption/desorption, SCR reaction, NH_3 oxidation, SO_2 oxidation, and sulfur deposition on Cu sites.

Results and Discussion

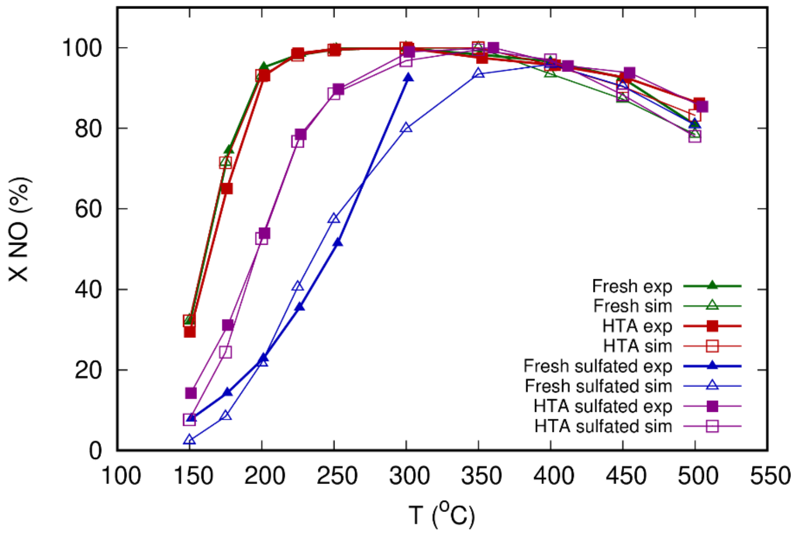

Figure 1. NOx conversion under standard SCR reaction conditions on fresh and hydrothermally aged (HTA) catalysts before and after SO_2 exposure. Full points – experiments, hollow points – simulation results.

First, a kinetic model that describes the changes in ZCuOH and Z_2Cu site concentrations during hydrothermal aging was developed using the information from catalyst characterization. The model can predict the rate of Cu site transformation depending on temperature and actual site concentrations[3]. Subsequently, a simulation study was conducted to describe the impact of sulfur poisoning on the fresh and hydrothermally aged samples' performance during standard the SCR reaction, Figure 1. The fresh and HTA samples show practically identical NO_x conversions as the dominant process in HTA is just a transformation from ZCuOH to Z_2Cu, and both sites exhibit similar SCR activity.

However, much larger differences exist after exposure to sulfur. The impact of sulfur poisoning is more pronounced on the fresh catalyst, leaving effectively only 4% of the Cu site activity compared to the fresh state. The hydrothermally aged is not affected as much, retaining 14% of the original activity. This trend is attributed to the transformation of ZCuOH sites to Z_2Cu sites during hydrothermal aging and the fact that Z_2Cu sites are less susceptible to sulfur poisoning than ZCuOH. This trend is further promoted by the higher activity of ZCuOH sites for SO_2 oxidation to SO_3 that binds more strongly to the catalyst surface.

The developed reaction kinetic model provides rational background for the observed phenomena and allows prediction of the catalyst performance in sulfur-containing environment depending on the actual distribution of ZCuOH and Z_2Cu sites in the catalyst as it may change during the catalyst lifetime.

References

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