

The Impact of Ammonium Nitrate Species on Low Temperature NOx Conversion Over Cu/CHA SCR Catalyst

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ABSTRACT

Cu/CHA catalysts have been widely used in the industry, due to their desirable performance characteristics including the unmatched hydrothermal stability. While broadly recognized for their outstanding activity at or above 200°C, these catalysts may not show desired levels of NOx conversion at lower temperatures. To achieve high NOx conversions it is desirable to have NO₂/NOx close to 0.5 for fast SCR. However even under such optimal gas feed conditions, sustained use of Cu/CHA below 200°C leads to ammonium nitrate formation and accumulation, resulting in the inhibition of NOx conversion.

In this contribution, the formation and decomposition of NH₄NO₃ on a commercial Cu/CHA catalyst have been investigated systematically. First, the impact of NH₄NO₃ self-inhibition on SCR activity as a function of temperature and NO₂/NOx ratios was investigated through reactor testing. Second, the formation of NH₄NO₃ was qualitatively measured through various adsorption and model reactions as well as its decomposition reactions by the temperature-programmed desorption (TPD). In addition, the transient formation and accumulation of NH₄NO₃ under relevant process conditions were tracked by *in situ* DRIFTS spectroscopy to identify its formation and accumulation mechanisms. Last, a kinetic model was built to estimate the NH₄NO₃ inhibition impact on NOx conversion. This work provides insights into the limiting processes and SCR reactions at low temperatures that are important for addressing future low temperature NOx conversion needs.

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1. INTRODUCTION

Selective catalytic reduction of nitrogen oxides (NOx) with NH₃ is a leading technology for lean-burn engines to meet the increasingly stringent environmental regulations worldwide. Among various SCR catalysts, Cu/CHA catalysts have been widely used in the industry nowadays, due to their excellent hydrothermal stability and outstanding activity at or above 200°C, even under standard SCR conditions [1, 2, 3].

On the other hand, the exhaust temperature is getting lower as a result of the increased fuel efficiency. For example, recent gains in fuel efficiency are translating into substantial exhaust temperature reductions, and future fuel efficiency improvements are underway, which are expected to translate into additional exhaust temperature reduction [4]. Sustainable low-temperature operation, i.e. below 200°C, is inherently challenging for all types of SCR catalyst. In order to achieve high NOx conversions, it is desirable to utilize the fast SCR reaction with NO₂/NOx close to 0.5, which is possible to achieve by DOC selection and optimization of its location. However even under such optimal gas feed conditions, sustained use of Cu/CHA below 200°C leads to ammonium nitrate formation and

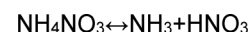
accumulation leading to the inhibition of NOx conversion [5, 6, 7]. In addition, the decomposition of accumulated NH₄NO₃ will lead to the formation of N₂O, an undesired greenhouse gas.

At temperatures below 200°C, the NH₄NO₃ is typically formed by a reaction of NO₂ and NH₃ in the ratio of 1:1. The NH₄NO₃ deposits cause fouling or masking of the pore channels of the catalyst and inhibit the SCR reaction, leading to its temporary deactivation. Note, the formation of NH₄NO₃ is favored by low temperature, therefore, the lower temperature tends to have more NH₄NO₃ formation and inhibition [5, 8].



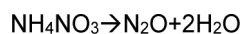
(R1)

There are at least three reactions for NH₄NO₃ removal: NH₄NO₃ sublimation (R2), thermal decomposition (R3) and reaction with NO (R4) [5, 8].

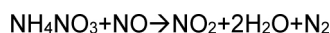


(R2)





(R3)



(R4)

Although many researchers have discussed NH_4NO_3 impact on Cu, Fe based zeolite as well as V-based SCR catalysts, few have been focused systematically on the small-pore Cu/CHA catalysts [8-9]. In this contribution, the impact of ammonium nitrate species on low temperature NOx conversion over a Cu/CHA SCR catalyst was investigated, and the formation of NH_4NO_3 was measured through various adsorption and model reactions by DRIFTS, or followed by TPD. Finally a model has been developed to quantify NH_4NO_3 impact on NOx conversion. This work provides new insights into NH_4NO_3 formation and its inhibition impact on SCR reactions at low temperatures, which are important for addressing future low temperature NOx conversion needs.

2. EXPERIMENTAL PROCEDURES

2.1 Catalyst Materials

Cu-SSZ-13 formulation used in this study, which was washcoated on a 300 cpsi cordierite substrate, was purchased from commercial sources. Cylindrical catalyst samples with 1" diameter 3" length were used for the performance evaluation in a laboratory reactor. The sample was degreened at 550°C for 4h in humidified gas feed (10% O_2 , 8% CO_2 , 7% H_2O with the balance of N_2).

2.2 Experimental Setup and Conditions

Experimental data were collected using a bench-flow reactor system, described in detail previously [10]. Simulated exhaust gases (200ppm NOx, 200ppm NH_3 , 10% O_2 , 8% CO_2 , 7% H_2O , balance N_2) were fed to the catalyst sample at a total flow rate of 26 slpm, corresponding to a gas hourly space velocity (GHSV) of approximately 40,000 h^{-1} . The effluent gas composition was analyzed by a high-speed MKS MultiGas 2030 FTIR.

2.3 Temperature Programmed Desorption (TPD)

TPD method was used to characterize the adsorption species including the formed NH_4NO_3 . Prior to TPD results, the sample was treated in base feed at 500°C for 30 min to clean the surface. After cooling down to 150°C, adsorption of individual species, or species in sequence, or co-feed species were performed; afterwards, the adsorbed species were cut-off and held for 20min for an isothermal desorption. Finally, temperature-programmed desorption was performed with a temperature ramp from 200 to 550°C at a rate of 10°C/min, under a gas mixture of 8% CO_2 , 7% H_2O and balance N_2 . Importantly, oxygen was excluded from the TPD gas mixture.

2.4 DRIFTS Characterization of Cu-SSZ-13

Cu-Zeolite powder samples scraped from the cores were loaded in a DRIFTS reactor cell (Nicolet 6700 spectrometer equipped with Praying Mantis high-temperature DRIFTS cell, Harrick temperature control box and gas manifold assembled in house), pre-treated at

500°C in 10% O_2/Ar for 30 min and subsequently cooled to 150°C. Then, background spectra were collected after the gas switched to 2% H_2O at 150°C for 30 min. Afterwards, either NH_3 or NOx was introduced to the surface individually, sequentially or in a co-feed way (200 ppm NH_3/Ar or 200ppm NOx/Ar) (200 ppm. All the adsorption and reaction tests were performed at 150 °C, in the presence of 2% H_2O . The DRIFTS spectra were recorded in the range of 4000-650 cm^{-1} at 64 scans with a resolution of 4 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1 Impact of NO_2/NOx ratio on NOx Conversion at Low Temperature

NO_2 sweep tests, with fixed NH_3 and NOx concentration ($\text{NH}_3=\text{NOx}=200\text{ppm}$) but varied NO_2/NOx ratios ranging from 0 to ~0.8, were performed on the catalyst at different temperatures. Time-on-stream outlet NOx, NH_3 and N_2O concentrations are plotted in Fig. 1. As expected, with increasing NO_2/NOx ratio from 0 to 0.5, NOx conversion gradually increased, and further increase in NO_2/NOx ratio led to decreased NOx conversion, due to the increased portion of fast SCR. N_2O formation, on the other hand, shows a trend of increase with increased NO_2/NOx ratio. It is worth noting that steady-state NOx reduction could not be achieved in some cases when NO_2/NOx ratios are high enough, such as, 0.5 at 163°C, 0.6 at 192°C and 0.84 at 235°C. This is due to the accumulation of NH_4NO_3 on the surface of the catalysts which inhibits the SCR reaction. The formation of NH_4NO_3 could be confirmed by the formation of N_2O upon a follow-up temperature ramping. Meanwhile, we will show you later the identification of NH_4NO_3 using IR spectroscopy.

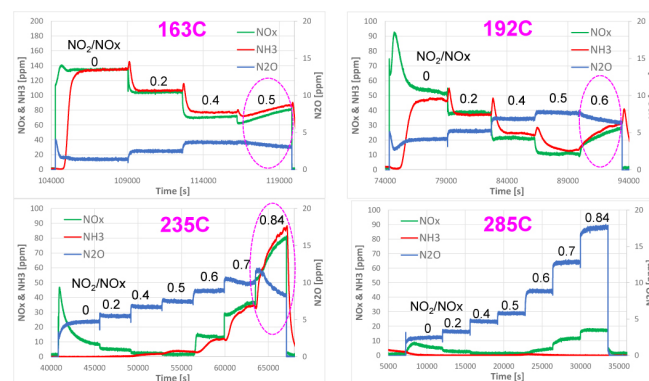


Figure 1. Time-on-stream reactor outlet gas concentrations at various temperatures (Feed $\text{NOx}=\text{NH}_3=200\text{ppm}$)

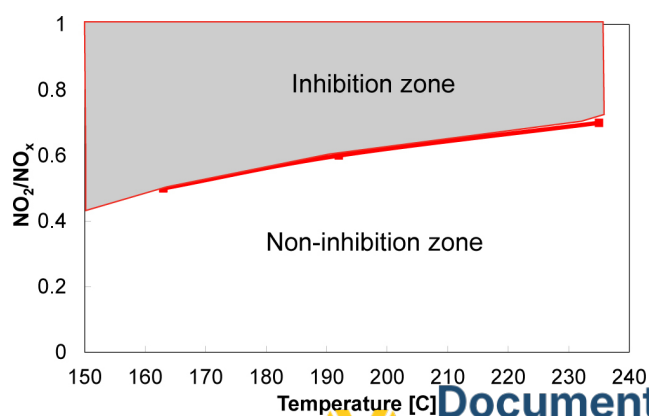


Figure 2. Mapping of NH_4NO_3 self-adsorption zone regarding NO_2/NOx ratio and temperature