

Using Transient FTIR Spectroscopy to Probe Active Sites and Reaction Intermediates for Selective Catalytic Reduction of NO on Cu/SSZ-13 Catalysts

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Introduction

Cu/SSZ-13 zeolite catalyst has been commercialized for selective catalytic reduction of NOx with ammonia (NH₃-SCR) in diesel vehicle after-treatment systems¹. In terms of reaction mechanisms, it has been frequently proposed that NH₂NO and NH₄NO₂ are the likely intermediates that decompose to N₂+H₂O. However, their detection via spectroscopy, and their detailed formation pathways, have not been established. It has been well accepted that under typical low-temperature SCR conditions, NH₃ is much more strongly adsorbed than NOx, which occupy both Cu Lewis acid sites (abbreviated as L-NH₃) and zeolite Brønsted acid sites (abbreviated as B-NH₃). The latter has been suggested to be much less reactive. In this work, we use NO+O₂ mixtures to titrate NH₃-saturated Cu/SSZ-13 under both continuous and pulsed modes, monitored with in situ time resolved DRIFTS, aiming to obtain further information about SCR mechanisms, particularly active Cu complexes and key intermediates. To separate key adsorbates spectroscopically, ND₃ instead of NH₃ was utilized in certain experiments.

Materials and Methods

The Cu/SSZ-13 catalyst was prepared by aqueous ion-exchange. A commercial H/SSZ-13 powder (Si/Al = 10) was first exchanged into NH₄/SSZ-13. Subsequently, Cu/SSZ-13 was obtained by exchanging with a Cu acetate solution. Copper content of the catalyst was 1.40 wt. % as determined by ICP-OES. Catalyst activity test was carried out on a fixed-bed quartz tube system. In situ DRIFT experiments were conducted with a Nicolet 6700 FT-IR spectrometer, equipped with an MCT detector and a Harrick reaction cell with ZnSe windows. Prior to the tests, the sample was pre-treated with 5% O₂/N₂ (100 ml/min) at 500 °C for 30 min. DRIFT spectra were typically recorded from 4000 to 400 cm⁻¹ by accumulating 5 scans with a resolution of 4 cm⁻¹.

Results and Discussion

NH₃-SCR reaction tests at space velocities relevant to application revealed over 95% NOx conversions between 250 and 550 °C with ~100% N₂ selectivity, demonstrating that the catalyst used here contains predominately isolated Cu-ions, thus highly suitable for fundamental mechanistic studies. At 250 °C, 500 ppm NH₃ was introduced to the Cu/SSZ-13 until saturation. At this point, 500 ppm NO/O₂ (100 ml/min) was continuously introduced and time series DRIFT spectra were recorded. **Figure 1a** presents selected spectra at different stages of the reaction. L-NH₃ disappears faster than B-NH₃, consistent with literature findings that the former has higher reactivity². To gain further kinetic details, their peak areas were integrated and ratioed against those at time zero as plotted in **Figure 1b**. B-NH₃ intensity starts declining only after the consumption of L-NH₃, which demonstrates that B-NH₃ serves as a reservoir for the reaction. L-NH₃ and B-NH₃ consumption rates were estimated. Importantly, the consumption rates for L-NH₃ become faster with reaction time, and B-NH₃ consumption

rates are the fastest (even though B-NH₃ is consumed later). It is due to an NH₃ inhibition effect, where Cu(II) sites with multiple NH₃ ligands have low SCR rates and Cu(II) sites depleted with NH₃ have high SCR rates.

In order to further explore the surface intermediate species during SCR reaction, the periodic transient FTIR experiments were carried out where pulses of NO were used to perturb steady-states. To circumvent potential vibration overlap between NH₃ and nitrite/nitrate surface species, ND₃ was used in these measurements. As shown in **Figure 2a**, NO introduction leads to the expected L-NH₃ intensity decrease, but unexpected B-NH₃ intensity increase. Such findings are consistent with a redox SCR mechanism proposed by Paulucci et al³ where the reduction half-cycle involves proton release, which interacts with NH₃ molecules to generate B-NH₃. As shown in **Figure 2b**, surface nitrates or NH₄NO₃ are not involved in the low-temperature redox reaction.

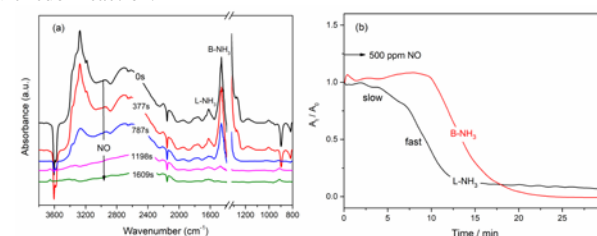


Figure 1a. Selected DRIFT spectra during NO titration on NH₃-equilibrated Cu-SSZ-13 at 250°C. **Figure 1b.** Time evolution of B-NH₃ and L-NH₃. A_t/A₀ is their related integrated peak areas normalized with those at time zero.

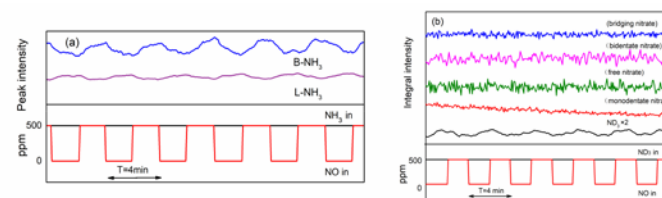


Figure 2a. The time evolution of the selected DRIFT spectra during NO+NH₃+O₂/NH₃+O₂ modulation experiment at 250 °C (T = 4 minutes). Representation of the pulse sequence (NH₃ in, NO in). Conditions: NH₃ (500 ppm), NO (500 ppm), O₂ (5 vol %) in N₂. **Figure 2b.** The same modulation experiment with Figure 2a but ND₃ instead of NH₃.

Significance

An important NH₃-inhibition effect is confirmed via spectroscopy in SCR. The titration results provide solid support for a redox reaction mechanism proposed recently. Nitrates are not involved in low-temperature SCR.

References

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