

Identification of two types of Cu sites and their unique responses to hydrothermal aging and sulfur poisoning

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Introduction

The Cu/chabazite (Cu/CHA) catalysts are widely used and proven selective catalytic reduction (SCR) catalysts for NO_x with NH₃ [1]. The Cu/CHA based SCR catalysts were shown to have robust NO_x conversion, compared to conventional zeolite based catalysts, even after extreme hydrothermal treatments, making Cu/CHA catalyst a prime candidate in aftertreatment applications where actively regenerated DPF approach is employed. Even though the NO_x conversion is minimally impacted over the real-world operated Cu/CHA catalysts, due to aftertreatment system design, the redox and acid sites were found to change significantly from laboratory simulated studies. Hydrothermal aging and sulfur poisoning were identified as two key mechanistic routes responsible for change in the nature and the amount of redox and acid site species.

The impact of hydrothermal treatment and sulfur poisoning on NO_x conversion, redox species and acid sites in Cu/CHA catalysts were empirically evaluated, mainly through the SCR related reaction studies. There are limited but rapidly growing number of publications on the spectroscopic characterization of the active species in Cu/CHA catalysts [2, 3], i.e. DRIFTS characterization studies indicated that Cu ions primarily positioned in the six-membered rings at low ion exchange levels and the cages at high ion exchange levels [3].

In this study, the susceptibility of different species in Cu/CHA to hydrothermal treatment and sulfur poisoning and their impact on NO_x reduction with NH₃ are discussed. Characterization of redox and acidic sites in Cu/CHA were carried out by DRIFTS technique using various probe molecules.

Materials and Methods

The small-pore Cu/Chabazite catalyst used in this work was purchased from commercial sources. Cylindrical core samples of 1"x3" size were treated at 550C, 700C or 800C for 4h, respectively, to generate samples of different hydrothermal aging conditions. Sulfation was done at 400C for 24h with 33 ppm SO_x (SO₂/SO_x=0.7) in the presence of H₂O, O₂ and CO₂. After various treatments, the catalysts were evaluated in terms of SCR performance, oxidation function and NH₃ storage, using the 4-step protocol (200ppm NO, 200ppm NH₃, 7%H₂O, 8% CO₂, 10%O₂ balanced by N₂, SV=40k) [4].

Powder samples, scraped from core samples after different treatments, were used for DRIFTS characterization (Nicolet 6700 spectrometer equipped with Praying Mantis DRIFTS cell). Samples were pretreated at 300C in 10% O₂/Ar and cooled to 35C. After background spectra collection, probe molecule NH₃ (200ppm NH₃/Ar) was introduced until saturated adsorption.

Results and Discussion

The activity of copper species, as probed by NO and NH₃ oxidation reactions, was found to decrease significantly upon progressive hydrothermal treatment and upon sulfation of Cu/CHA catalyst. Under SCR conditions used, hydrothermal aging and sulfur poisoning also negatively affect NO_x conversion, especially at low temperatures as shown in Fig.1 (left). The performance results indicate significant degradation of active sites upon various treatments.

Zeolite framework vibrations absorb IR radiation around 800 and 1050 cm⁻¹, assigned to symmetric and asymmetric T-O-T stretching vibrations. Ion exchange of zeolites with transition metal ions causes the perturbation of the T-O-T bonds, leading to absorption in the range of 850 to 1000cm⁻¹ (ascribed to the perturbed asymmetric T-O-T vibration), depending on the type of metal ions. The perturbation bands reveal the types of copper species that are associated or interacted with the zeolite framework. The absorption bands at 900 and 950cm⁻¹ can be correlated to the presence of two types of Cu species in Cu/CHA (Figure 1) [3]. Upon hydrothermal treatment, the number of type 2 Cu species decreased with a concomitant increase in type 1 species, indicating the latter species to be relatively more stable. Furthermore, the type 2 copper species were more strongly affinitive to sulfur, as indicated by insignificant absorption of corresponding band, compared to type 1 copper species after sulfation, as shown in Fig.1 (right). In other words, the strong interaction of type 2 Cu with sulfur weakens or diminishes its interaction with zeolite framework.

From the qualitative correlation of changes in performance and number and type of copper active species as identified by DRIFTS it will be argued that type 2 copper species are relative more active for various reactions especially oxidation function, but are more vulnerable to hydrothermal and sulfation treatments.

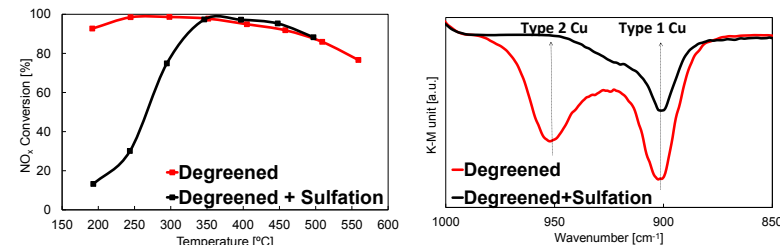


Figure 1. SCR performance (left) and DRIFTS spectra of Cu species (right) for Cu/Chabazite catalyst before and after sulfur poisoning

Significance

This contribution furthers the understanding of the active sites in Cu/CHA, an area which is actively pursued by various research organizations across the world.

References

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