Development of SSZ-13 based sulfur resistant NH_3-SCR catalysts

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Introduction

The ammonia-selective catalytic reduction (NH_3-SCR) of NOx is a widely used technology for the reduction of NOx emissions in stationary sources (gas-, oil-, and coal-power plants) and mobile sources (e.g., diesel engines). Previous studies have shown that the activity of SCR catalysts depends on a wide parameter space including the catalyst type (i.e., V_2O5/TiO_2 vs. zeolites), metal type, synthesis method, and reaction parameters (flue gas composition, reaction temperature, and space velocity). Moreover, the presence of excess O_2, SO_2 and H_2O vapor in combustion exhaust affects both catalyst selectivity and stability at high and low temperatures.

Many studies have shown that zeolites are promising catalysts to be operated under coal combustion flue gas conditions. Our previous work indicates that SSZ-13 based zeolite catalyst own higher thermal stability and NO_x conversion than other zeolite catalysts in an ideal flue gas condition (NO, NH_3, O_2 and N_2) [1]. However, SO_2 and H_2O vapor effect have not yet been considered in the reaction system. In this work, SSZ-13 catalysts loaded with Cu, Fe, Ce are synthesized and characterized to test NH_3-SCR activity under SO_2 and H_2O feed conditions. Catalysts with different sulfur resistance will be studied to explore the possible deactivation mechanism for further catalysts design.

Materials and Methods

The ion-exchanged SSZ-13 catalysts were prepared using a variation of our previous reported method [1]. The experiments were run in a fixed bed continuous-flow reactor, where the NO conversion was measured by the quadruple mass spectrometer. All catalytic reactions were performed using a feed stream containing 500ppm NO, 500ppm NH_3, 5% O_2, 5% CO_2, 8% H_2O(when used), 500ppm SO_2(when used), and balance N_2. The gas hourly space velocity was 40,000 h^{-1}. The NH_3-SCR activity of all samples was tested from 150 to 450 °C, with 100 °C increments.

Results and Discussion

Figure 1a shows the NO conversion for catalysts under simulated flue gas conditions. Without metal loading, H-SSZ-13 is found to have no catalytic activity. After ion-exchanging with Cu, Fe and Ce, the NO conversion of SSZ-13 catalysts jump to more than 80% in a high temperature window (350-450 °C). Moreover, Cu-SSZ-13 show more than 80% NO conversion in a low temperature window 150-250 °C while the NO conversions on other catalysts gradually drop down to less than 30%. Interestingly, the bi-metal exchanged Ce-Fe-SSZ-13 catalyst shows higher catalytic activity than either single metal catalyst, which is probably due to a synergy effect between Fe and Ce in NH_3-SCR reaction system [2].

The NH_3-SCR reaction results with SO_2 and H_2O in the feed are shown in **Figure 1b.** All catalysts are found to deactivate at low reaction temperatures with the addition of SO_2 and H_2O vapor. Among them, Cu-SSZ-13 shows the best poisoning resistance and keeps more than 90% NO conversion at high temperature. At low temperature, catalysts deactivate more than at high temperature, which might be due to the formation of $(NH_4)_2SO_4$ on the catalyst [3]. Our XPS results support the possible formation of $(NH_4)_2SO_4$, indicating that both NH_4^{1+} and SO_4^{2-} present on the surface of the catalysts. Detailed deactivation mechanism for different metal loading SSZ-13 catalysts will be explored.

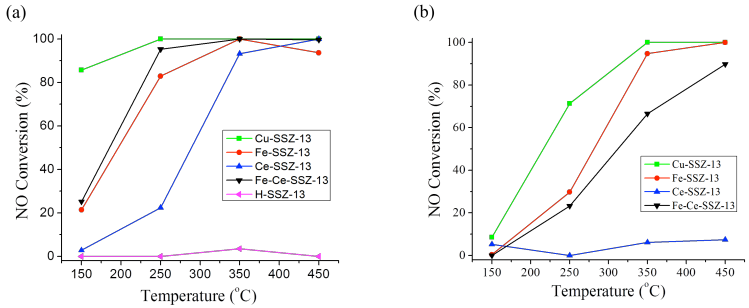

Figure 1. NH_3-SCR activity a) without H_2O or SO_2, b) with H_2O and SO_2

Significance

Cu-SSZ-13 has excellent NH_3-SCR activity and preform relatively high sulfur poisoning resistance.

References

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