Mechanistic Evaluation of the Low Temperature Activity of Transition Metal Exchanged Zeolite SCR Catalysts

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Introduction

Selective catalytic reduction (SCR) of NOx with urea over transition metal (Fe or Cu) exchanged zeolite catalysts is one of the leading technologies for NOx emission control for diesel engines. The choice of transition metal between Cu and Fe has a significant impact on the transient performance and the steady state catalytic activity of the catalyst. Grossale, et al. [1] have shown, that for Fe SCR systems, the performance of the catalyst at 250 °C goes through a maximum conversion during the first 10 minutes following the inclusion of NH_3. Cu systems do not display the same behavior. In addition, Fe and Cu zeolite SCR catalysts exhibit different performance depending on the NO:NO_2 ratio of the exhaust gas. Fe zeolite catalysts show a significant improvement in low temperature activity with the addition of NO_2 to the feed gas up to a maximum conversion at a 1:1 NO:NO_2 ratio. Cu catalysts, however, are less dependent on the NO:NO_2 ratio with high conversion in NO only feeds [2]. A fundamental understanding of the underlying SCR reaction mechanisms of Cu and Fe catalysts is therefore important for the development of engine calibrations and urea dosing strategies for these catalysts. In this study, surface adsorption FTIR spectroscopy will be used to evaluate the transient response and the impact of NO:NO2 ratio of the catalysts.

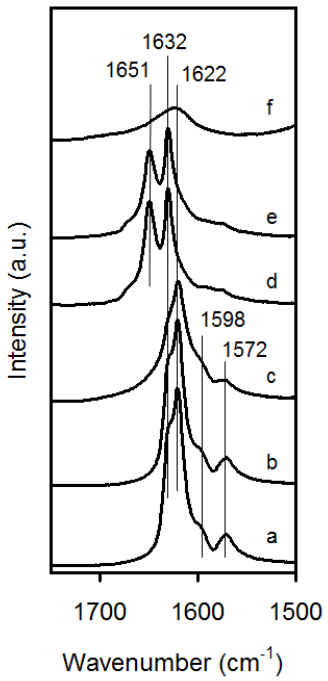
Materials and Methods

Transition metal (Cu or Fe) was introduced onto zeolite by ion-exchange. The catalysts are hydrothermally treated with 4.5% H_2O in air at 670 °C for 2 hours to be stabilized. Catalysts coated on monoliths were tested in a flow reactor at a space velocity of 30,000 h^{-1} with a gas composition of 350 ppm NH_3 and NO, 14%O_2, 4.6% H_2O, 5%CO_2 in N_2. Powder catalyst samples are pressed into 10 mg, 1 cm diameter pellets and mounted in a FTIR cell. The cell is purged for 1 hour at 500 °C in an 8% O2 in N_2 gas stream to remove adsorbed water. The cell is cooled and held at 200 °C. FTIR spectra are recorded every 2 minutes when the sample is exposed to different gas mixtures.

Results and Discussion

FTIR spectra revealed that the surface adsorption complexes and their formation kinetics on the Cu/zeolite and Fe/zeolite catalysts were noticeably different. When the Cu/zeolite was exposed to a mixture of (350 ppm NO + 14% O_2), IR bands at 1632, 1622, 1598, and 1572 cm^{-1} emerged gradually and reached saturation in about 30 minutes (Fig. 1a). These IR bands were stable with little change of their intensities upon subsequent purging (Fig. 1b). When the Fe/zeolite was exposed to the same gas mixture, however, an IR band at 1632 cm^{-1} appeared immediately and almost reached saturation in 6 minutes. Meanwhile, an IR band at 1651 cm^{-1} emerged slowly in the first 4 minutes but rose rapidly and reached its peak intensity in 10 minutes. After 10 minutes exposure, the intensity of the band at 1651cm^{-1} was actually higher than that of the band at 1632 cm^{-1}. Further extending the exposure time to 30 minutes led to a gradual decrease of the band at 1651 cm and a slight increase of the intensity at 1632cm^{-1} (Fig 1d). Upon subsequent purging with 14% O_2, the intensities of both bands decreased slightly with the change of band at 1651 cm^{-1} being more pronounced (Fig 1e).

The differences between the two catalysts are further displayed by their IR spectra after exposing the catalysts to a full gas mixture of (350 ppm NO + 350 ppm NH_3 + 14% O_2). On the Cu/zeolite catalyst, the IR bands at 1632, 1622, 1598, and 1572 cm^{-1} were still apparent although their intensities were slightly lower (Fig 1c). In contrast, on the Fe/zeolite catalyst, the IR bands at 1651cm^{-1} and 1632 cm^{-1} almost vanished in 10 minutes resulting a broad band at 1622 cm^{-1} (Fig 1f).



Clearly the FTIR study demonstrates that the Cu/zeolite and the Fe/zeolite catalyst have different reactivity in catalyzing NO+O_2 oxidation, a key step in the SCR reactions. The Cu/zeolite catalyst shows higher oxidation propensity than the Fe/zeolite catalyst, hence exhibiting less dependency on the NO:NO_2 ratio in the feed gas. This study also indicates that although highly reactive surface compounds can be formed on an NH_3-free Fe/zeolite catalyst, those surface compounds do not exist on the catalyst in the presence of NH_3.

Significance

Surface chemisorption FTIR study reveals the mechanistic difference between the Cu/zeolite and the Fe/zeolite catalysts in catalyzing the SCR reactions. The insights developed here is valuable for the optimizing engine calibrations and urea dosing strategies for each catalyst system.

Figure 1. FTIR spectra of surface adsorption complexes at 200 °C upon exposing the Cu/zeolite catalyst to (a) 350ppm NO + 14% O_2 for 30min; (b) subsequently purge with 14% O_2 for 30min; (c) then under flow of 350ppm NO + 350ppm NH_3 +14% O_2 for 30min; and the Fe/zeolite catalyst to (d) 350ppm NO + 14% O_2 for 30min; (e) subsequently purge with 14% O_2 for 30min; (f) then under flow of 350ppm NO + 350ppm NH_3 +14% O_2 for 30min.

References

1. Grossale, A., Nova, I., and Tronconi, E. *Catal. Today* 136, 18 (2008).
2. Kröcher, O. in "Studies of Surface Science and Catalysis (Aspects of Catalyst Development for Mobile Urea-SCR Systems – From Vanadia-Titania Catalysts to Metal Exchanged Zeolites)" (P. Granger and V. Pârvulescu, Eds.) Vol. 171 p. 261, 2007.