NH_3-SCR on fresh and hydrothermally aged Fe/SSZ-13 catalysts

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Introduction

With the successful implementation of Cu/SSZ-13 (a small pore zeolite with Chabazite (CHA) structure) as part of the emission control systems for diesel passenger vehicles, and light- and medium-duty trucks in the U.S. and Europe, there has been a new surge of research interest in NH_3-SCR over Cu-Chabazite [1]. While Cu/SSZ-13 has been extensively studied, systematic investigations for Fe/SSZ-13 as NH_3-SCR catalysts are still lacking. In this study, we investigated SCR kinetics on both freshly prepared and hydrothermally aged Fe/SSZ-13 catalysts with various Si/Al ratios (5, 12 and 35) and Fe loadings, and the nature of Fe species with Mössbauer and Infrared Spectroscopies.

Materials and Methods

SSZ-13 was synthesized hydrothermally using a method recently developed by Deka et al. [2]. Fresh Fe/SSZ-13 was synthesized by ion-exchanging NH_4/SSZ-13 with $FeSO_4$ solution at 80 °C and pH ~3.0 for 1h, under a N_2 atmosphere. Hydrothermal treatment was conducted at 800 °C for 16 h in the presence of 20% O_2 and 10% H_2O. Standard NH_3-SCR and NO/NH_3 oxidation reactions were measured using a plug-flow reaction system [3] descried previously. The feed gas contained 350 ppm NO, 350 ppm NH_3, 14% O_2, 2.5% H_2O and balance N_2. Typical GHSV was 200,000 h^{-1}.

Routine characterizations of the catalysts included BET surface area/pore volume measurements, X-ray diffraction (XRD) for crystallinity, and ICP analyses for Fe loadings and Si/Al ratios. To elucidate the nature of the Fe species, catalysts were further characterized with H_2 temperature programmed reduction (H_2-TPR), CO/NO chemisorption by infrared spectroscopy (FTIR), ^{57}Fe Mössbauer spectroscopy, and nuclear magnetic resonance (NMR).

Results and Discussion

Surface area/pore volume and XRD measurements showed that our Si/Al = 5 samples experienced moderate crystallinity decrease after hydrothermal aging while the Si/Al = 12 and 35 samples maintained excellent crystallinity. Iron oxides were not detected on any of the samples before and after hydrothermal aging.

Figure 1 presents NO and NH_3 conversions as a function of the temperature in NH_3-SCR on our fresh and aged Fe/SSZ-13 (Si/Al = 12, Fe/Al = 0.2) samples. The fresh sample maintained very good SCR activity and selectivity between 300 and 550 ºC. The hydrothermally aged sample maintained much of the activity and selectivity above ~350 ºC.

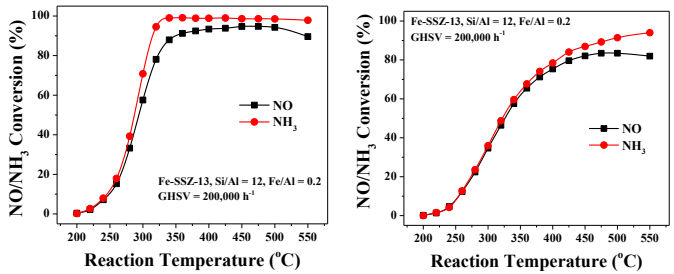

Figure 1. NO and NH_3 conversions as a function of the temperature on fresh (left) and aged (right) Fe/SSZ-13 (Si/Al=12, Fe/Al = 0.2) samples.

Mössbauer measurements (**Figure 2**) showed that in the fresh sample both Fe^{2+} (11 %) and Fe^{3+} (89 %) ions are present. Among the Fe^{3+} ions, 37% are in the form of isolated monomers, 43 % are dimers and the rest ~8 % are in Fe_2O_3 clusters. Upon aging, some Fe^{2+} further converted to Fe^{3+}, however the monomeric and dimeric Fe^{3+} ions remained stable without converting to Fe_2O_3 clusters. This general trend was confirmed from Mössbauer measurements at various temperatures (ambient, 77 K and 6 K) and on other samples with different Si/Al ratios and Fe loadings.

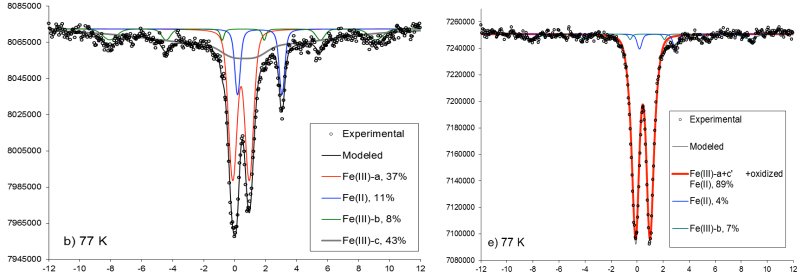

Figure 2. Mössbauer spectra of fresh (left) and aged (right) Fe/SSZ-13 (Si/Al = 12, Fe/Al = 0.2) samples measured at 77 K.

Significance

Highly active Fe/SSZ-13 SCR catalysts are readily synthesized using solution ion exchange. Their stability and high selectivity at elevated temperatures (> 350 ºC) indicate that they can be used as high-temperature SCR catalysts.

References

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