NH₃-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 NH₃-SCR over Cu-Chabazite [1]. While Cu/SSZ-13 has been extensively studied, systematic investigations for Fe/SSZ-13 as NH₃-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 NH₄SSZ-13 with FeSO₄ solution at 80 °C and pH ~3.0 for 1h, under a N₂ atmosphere. Hydrothermal treatment was conducted at 800 °C for 16 h in the presence of 20% O₂ and 10% H₂O. Standard NH₃-SCR and NO/NH₃ oxidation reactions were measured using a plug-flow reaction system [3] described previously. The feed gas contained 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O and balance N₂. 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 H₂ temperature programmed reduction (H₂-TPR), CO/NO chemisorption by infrared spectroscopy (FTIR), ⁵⁷Fe 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 NH₃ conversions as a function of the temperature in NH₃-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 °C. The hydrothermally aged sample maintained much of the activity and selectivity above ~350 °C.

Mössbauer measurements (Figure 2) showed that in the fresh sample both Fe⁷⁺ (11 %) and Fe⁹⁺ (89 %) ions are present. Among the Fe⁷⁺ ions, 37% are in the form of isolated monomers, 43% are dimers and the rest ~8% are in Fe₂O₃ clusters. Upon aging, some Fe⁷⁺ further converted to Fe⁹⁺, however the monomeric and dimeric Fe⁹⁺ ions remained stable without converting to Fe₂O₃ 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.

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

References