

Impact of Accelerated Hydrothermal Aging on Structure and Performance of Cu-SSZ-13 SCR Catalysts

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ABSTRACT

In this contribution, nuanced changes of a commercial Cu-SSZ-13 catalyst with hydrothermal aging, which have not been previously reported, as well as their corresponding impact on SCR functions, are described. In particular, a sample of Cu-SSZ-13 was progressively aged between 550 to 900°C and the changes of performance in NH₃ storage, oxidation functionality and NO_x conversion of the catalyst were measured after hydrothermal exposure at each temperature. The catalysts thus aged were further characterized by NH₃-TPD, XRD and DRIFTS techniques for structural changes. Based on the corresponding performance and structural characteristics, three different regimes of hydrothermal aging were identified, and tentatively as assigned to “mild”, “severe” and “extreme” aging. Progressive hydrothermal aging up to 750°C decreased NO_x conversion to a small degree, as well as NH₃ storage and oxidation functions. However, an unexpected increase in oxidation performance was observed upon further aging at 800 and 850°C. This phenomenon was probed and explained based on the changes in the nature of copper species in the Cu-SSZ-13 catalyst. Further aging above 850°C eventually resulted in catalyst structure collapse, leading to the loss of all the catalyst functions.

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1. INTRODUCTION

The recent discovery of Cu-chabazite (Cu-CHA) catalysts advanced the commercialization of urea-SCR technology to meet the current and emerging NO_x regulations, due to the wide operation temperature window, low NH₃ slip, and significantly enhanced thermal stability [1]. In several SCR architectures, such as D₂C+DPF+SCR, LNT+SCR or SCR on filter, SCR catalyst is periodically exposed to high temperatures above 600°C during deSO_x or DPF regeneration [2]. Despite the fact that the steady-state performance of Cu-CHA catalysts is impacted to a limited extent, the underlying functions of the catalyst such as, NH₃ storage and oxidation functions, are irreversibly degraded [3, 4, 5, 6, 7]. The above-mentioned changes in catalyst functions have to be understood in order to model the deactivation processes and build robust aftertreatment controls

increment of 50°C, and maintained at each temperature for 4h in humidified gas feed (10% O₂, 8% CO₂, 7% H₂O with the balance of N₂).

2.2. Experimental Setup and Conditions

Experimental data were collected using a bench-flow reactor system, described in detail previously [3]. Simulated exhaust gases (200ppm NO, 200ppm NH₃, 10% O₂, 8% CO₂, 7% H₂O, balance N₂) were fed to the catalyst sample at a total flow rate of 26 slpm, corresponding to a gas hourly space velocity (GHSV) of approximately 40,000 h⁻¹. The effluent gas composition was analyzed by a high-speed MKS MultiGas 2030 FTIR. 4-step SCR test protocols were used to evaluate the performance of the catalyst after each aging [2, 8].

2. EXPERIMENTAL PROCEDURES

2.1. Catalyst Materials

Cu-SSZ-13 formulation used in this study, which was washcoated on a 300 cpsi cordierite substrate, was purchased from commercial sources. Cylindrical catalyst samples with 1" diameter 3" length were used for the performance evaluation in a laboratory reactor. One sample was progressively heated between 550 to 900°C with an

2.3. NH₃ Temperature Programmed Desorption (NH₃-TPD)

Strength and distribution of the acid sites, which depicts the unique characteristics of Cu-SSZ-13 catalyst [3], were probed by NH₃-TPD technique. Prior to NH₃-TPD, the NH₃ adsorption was carried out by saturating a core sample with 200 ppm NH₃ at approximately 200°C followed by the desorption under a gas mixture of 8% CO₂, 7% H₂O and balance N₂ with a temperature ramp from 200 to 550°C at a rate



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of 10°C/min. Importantly, oxygen was excluded from the TPD gas mixture, to avoid oxidation of ammonia desorbing at elevated temperatures.

2.4. XRD Analysis of Cu-SSZ-13

XRD scans of the Cu-SSZ-13 samples hydrothermally aged at different temperatures were performed on a Panalytical Xpert diffractometer using CuK α radiation ($\lambda=1.540598$ Å), and an X'Celerator detector. XRD patterns were continuously collected within a 2θ range of 2-60° at constant temperature 500°C in air flow.

2.5. DRIFTS Characterization of Cu-SSZ-13

Cu-SSZ-13 powder used for DRIFTS analysis was scraped from cores of the same commercial catalyst, loaded in a ceramic boat and hydrothermally aged in a progressive manner in the reactor under identical conditions as used for the core sample. The aged powder samples were loaded in a DRIFTS reactor (Nicolet 6700 spectrometer equipped with Praying Mantis DRIFTS cell and gas manifold), pretreated at 500°C in 10% O₂/Ar for 30 min and subsequently cooled to 50°C. After background spectra collection in pure Ar, probe molecule NH₃ (200ppm NH₃/Ar) was introduced for around 2h until saturation. DRIFTS spectra were continuously collected during the whole adsorption process, however, only the spectra upon saturation, which are expected to capture the entire range of detectable sites, were shown here.

3. RESULTS AND DISCUSSION

3.1. Impact of Hydrothermal Aging on NO_x Conversion

90% NO_x conversion in a wide temperature range between 250°C and 450°C, suggesting robustness of NO_x conversion to thermal exposure. NO_x conversion significantly dropped after >850°C hydrothermal treatment due to the structure collapse of the catalyst, which is confirmed by XRD test (results shown later).

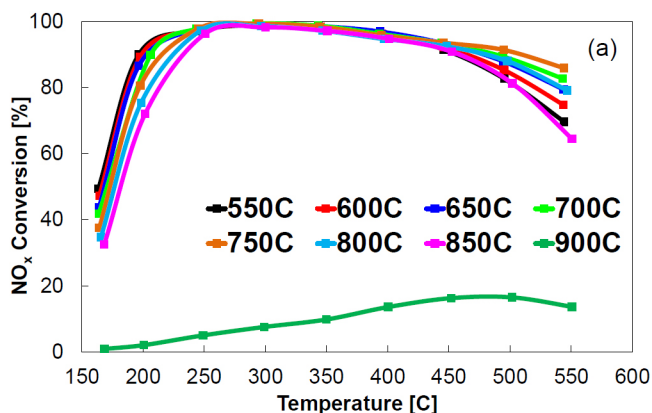


Figure 1.

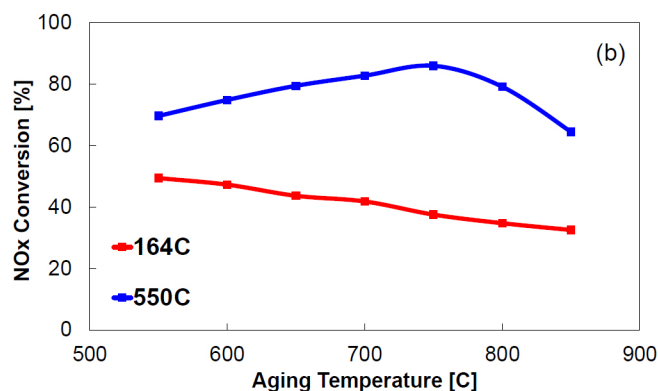


Figure 1. (cont.) (a) NO_x conversion on catalysts aged at different temperatures, (b) NO_x conversion at 164°C and 550°C as a function of aging temperatures

Although high NO_x conversion remains in the medium temperature range upon thermal exposure to 850°C, NO_x conversion at both low and high temperatures is still impacted. As summarized in Fig.1 (b), NO_x conversion at low temperature 164°C decreases monotonically, from ~50 to 30%, upon progressive hydrothermal aging up to 850°C, while NO_x conversion at high temperature 550°C increases first from 70 to 86% upon aging at 750°C, and decreases to 65% upon further aging to 850°C.

At temperatures above 550°C, NO_x conversion is primarily controlled by the selectivity of NH₃ reaction with NO_x vs. oxygen. In other words, direct oxidation of NH₃ by oxygen limits availability of NH₃ for NO_x reduction, especially when ammonia is present in stoichiometric quantities only, as was the case in this study. We therefore hypothesized that the changes in NO_x conversion efficiency at 550°C, as shown in Figure 1b, can be explained based on the changes in the ammonia oxidation abilities of the catalyst. This assumption is examined in the following section via direct measurements of the NH₃ oxidation function.

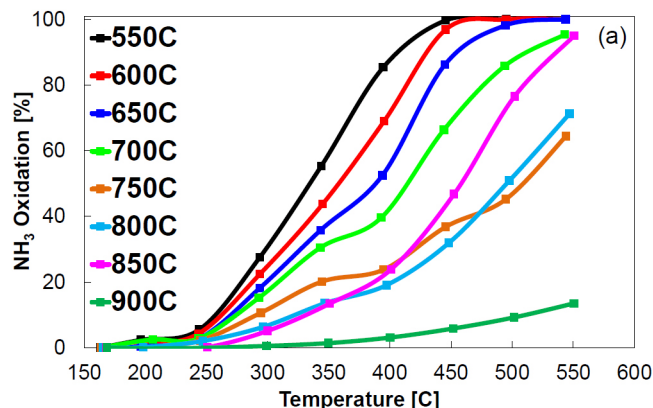


Figure 2. (a) NH₃ oxidation on catalysts aged at different temperatures, (b) NH₃ conversion at 300°C and 550°C as a function of aging temperatures