

Thermal durability and deactivation of Cu zeolite SCR catalysts

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Introduction

Diesel vehicles offer performance and fuel efficiency benefits over gasoline vehicles however the difficulty in controlling NOx emissions to meet U.S. Federal Tier 2 and California LEV II regulations may limit their use. Additionally, heavy duty diesel vehicles will be required to meet more stringent NOx emission regulations in 2010. Recently, there has been significant interest in the selective catalytic reduction (SCR) of NOx with ammonia for mobile source NOx control to enable application of the diesel powertrain. Compared to alternative technologies such as the NOx adsorber, ammonia SCR operates over a broader temperature range and does not require expensive platinum group metals.

Transition metal/zeolite catalysts are more attractive than V/Ti catalysts for SCR on mobile diesel engines due to the requirement to withstand temperature excursions in excess of 700°C. Fe-zeolite catalysts have been investigated by many research groups [1, 2] but their main disadvantage is low NOx conversion at operating temperatures below 250°C for a feed gas with low NO₂ concentration. In contrast, Cu-zeolite catalysts are effective at temperatures as low as 200°C in an NO₂ free feed gas. However, there is relatively little information available on the durability and deactivation mechanisms of Cu-zeolite catalysts, especially after extended aging at temperatures above 650°C. Over the full useful life of a vehicle, the exhaust system could be exposed to these high temperatures for extended time periods due to the need to actively regenerate particulate filter devices. The purpose of this investigation is to evaluate the thermal durability of Cu-zeolite over long term hydrothermal aging at 670°C. Additionally, deactivation mechanisms are clarified with several characterization technologies.

Materials and Methods

A proprietary NH₄-zeolite powder was ion-exchanged with Cu(NO₃)₂. The catalytic material was coated on a cordierite honeycomb monolith with a cell density of 400 cpsi. The coated honeycomb was cut into 1" diameter x 1" length cores. All cores were aged together in a tube furnace in air with 4.5% H₂O for up to 250 hours. At designated aging intervals, one core was removed to measure NOx conversion and NH₃ storage capacity in a laboratory reactor. Catalyst was also scrapped from each core and analyzed with XRD, BET, and H₂-TPR techniques. Acidity was characterized with infrared spectroscopy of adsorbed pyridine.

SCR activity was measured with gas conditions of 350ppmNH₃, 350ppmNO, 10%O₂, 4.6% H₂O and 5%CO₂ at a gas hourly space velocity of 100,000 h⁻¹. NH₃ storage capacity was measured at a given temperature by pre-adsorbing NH₃ at the specified temperature from a gas with a composition of 350ppm NH₃, 10%O₂, 4.6%H₂O, 5%CO₂, balance N₂ and gas hourly space velocity of 30,000 h⁻¹. When the outlet NH₃ reached 350ppm, the gas was switched to 175ppm NO, 175ppm NO₂, 10%O₂, 4.6%H₂O, 5%CO₂, and balance N₂ at gas hourly space velocity of 30,000 h⁻¹ and the NOx consumption was monitored. When the outlet NOx reached 350ppm, the total adsorbed NH₃ was calculated from the measured integrated NOx conversion.

Results and Discussion

DeNOx reaction rate constant at 200°C, with the assumption that SCR reaction rate is first order in NO and independent of NH₃ [3], is calculated and shown in Figure 1 as a function of aging time. Accordingly, the NH₃ storage capacity related to the fresh Cu-zeolite catalyst is also shown in Figure 1. The rate constant decreased rapidly from 0 to 64 hours but then decreased gradually between 64 and 250 hours. The initial rapid deactivation is mainly attributed to the loss of zeolite acidity as demonstrated by a significant decrease in both the NH₃ storage capacity and the number of Bronstead acid sites (as measured in the IR spectrum of adsorbed pyridine). The acidity loss arises from diminished zeolite crystallinity and surface area (measured with XRD and BET) which may be due to zeolite dealumination. At longer aging times, the deactivation related to Cu sintering and/or Cu interaction with zeolite is expected in addition to acidity loss. However, the gradual reaction rate decrease over the 64h to 250h interval suggests these mechanisms caused little deterioration. Therefore, it is concluded that the key issue for longevity under current aging conditions is the deactivation due to zeolite acidity loss during the initial 64 hours.

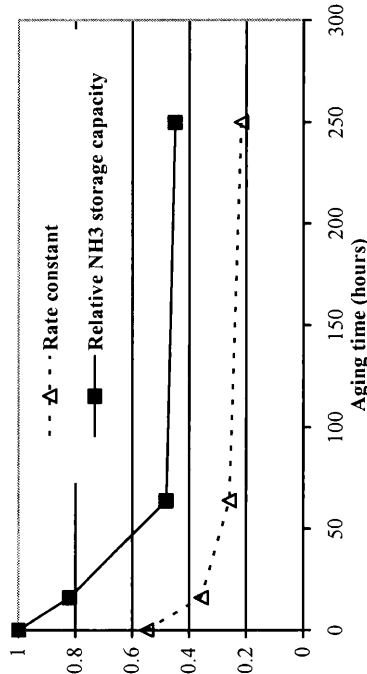


Figure 1. Rate constant and relative NH₃ storage capacity at 200°C vs. aging time at 670°C.

Significance

Cu-zeolite catalysts were investigated in a systematic way for longevity and deactivation mechanisms under an aging condition encountered in practical diesel vehicles. DeNOx performance was characterized under accelerated aging conditions as a function of aging time up to 250 hours. Also, key deactivation mechanisms were identified which will be useful for future development of more robust Cu-zeolite catalysts.

References

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