

Why Cu- and Fe-Zeolite SCR Catalysts Behave Differently At Low Temperatures

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ABSTRACT

Cu- and Fe-zeolite SCR catalysts emerged in recent years as the primary candidates for meeting the increasingly stringent lean exhaust emission regulations, due to their outstanding activity and durability characteristics. It is commonly known that Cu-zeolite catalysts possess superior activity to Fe-zeolites, in particular at low temperatures and sub-optimal NO_2/NO_x ratios. In this work, we elucidate some underlying mechanistic differences between these two classes of catalysts, first based on their NO oxidation abilities, and then based on the relative properties of the two types of exchanged metal sites. Finally, by using the ammonia coverage-dependent NO_x performance, we illustrate that state-of-the-art Fe-zeolites can perform better under certain transient conditions than in steady-state.

1. INTRODUCTION

A new generation of zeolite-based catalysts, which evolved in recent years, represents a very attractive alternative to the vanadia/titania-based materials, traditionally used for the selective catalytic reduction of NO_x by ammonia (SCR). In particular, Cu- and Fe-based zeolite formulations have attracted substantial practical interest, due to their remarkable activity and durability characteristics [1, 2]. It has been well documented that steady-state low-temperature activity of the state-of-the-art Cu-zeolite formulations is by far superior to that of Fe-zeolites at NO_2/NO_x ratios below 0.5 [1,2,3]. However, it is often difficult to approximate steady-state SCR performance in transient operation due to a large ammonia storage capacity of the present zeolite-based SCR catalysts. It is well known that NO_x conversion can have a complex relationship to NH₃ storage. Depending on the duty cycle and reductant injection strategy, SCR catalysts often operate with the amounts of ammonia on their surface substantially below steady-state coverage levels.

In this work, we have focused on developing an understanding of the details of the behavior of both Cu- and Fe-zeolite SCR catalysts, to bridge the gap between their transient and steady-state performance.

2. EXPERIMENTAL DETAILS

2.1. CATALYST MATERIALS

State-of-the-art Fe- and Cu-zeolite catalysts were provided by Johnson Matthey, supported on 400cps cordierite substrates. The two materials differed not only by the type of exchanged metal, but in several other regards, such as the type of zeolite framework. However, the qualitative behaviors we describe are common among the various Fe- and Cu-zeolite materials we have characterized to date.

Cylindrical samples of 1" diameter and 3" length were used for the reactor testing. Prior to testing, every sample was degreened, typically for 2-5h at 600°C, or aged for 100h at 700°C in the presence of a gas stream containing 10% O₂, 8% CO₂, 7% H₂O with the balance of N₂.

2.2. EXPERIMENTAL SETUP AND CONDITIONS

The experimental data in this work were collected using a bench-flow reactor system with rapid transient capabilities. Gas composition analysis was performed using fast-speed model of the MKS MultiGas 2030 FTIR. All the gas lines in the system were temperature-controlled, to minimize adsorption of NH₃ and H₂O. The reactor tube was made of fused silica to avoid parasitic oxidation of NH₃ at high temperatures.

Synthetic exhaust gas was supplied to the catalyst sample at a total flow rate of 26 slpm, resulting in the gross hourly space

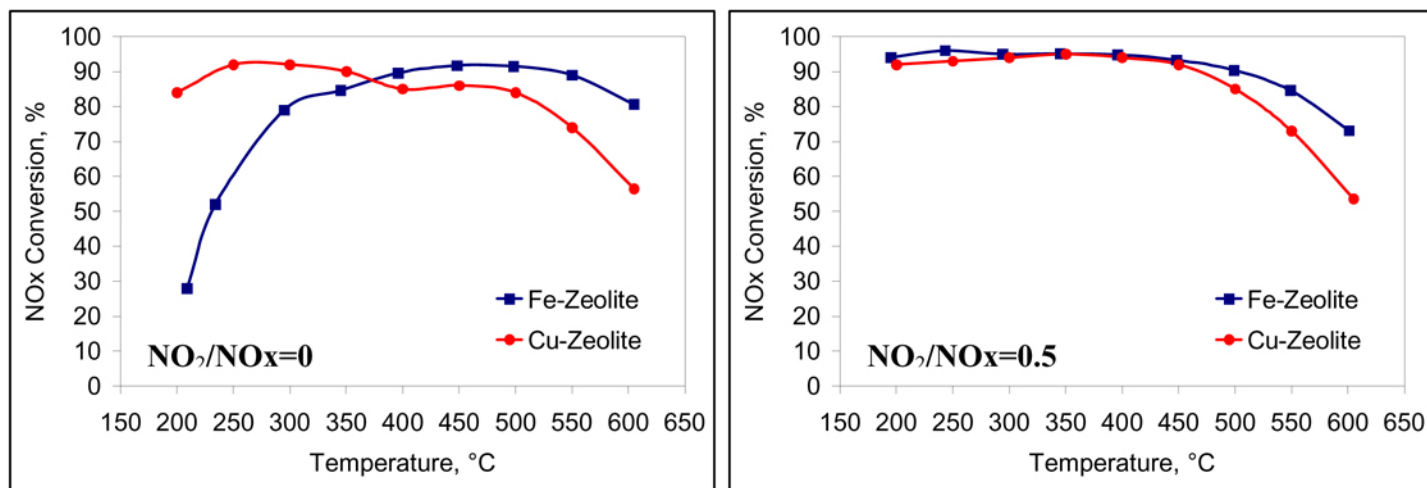


Figure 1. Steady-state NOx conversion on degreened Cu- and Fe-zeolite catalysts at different NO₂/NO_x ratios

velocity of approximately 40,000 h⁻¹. Unless specifically noted in the text, the base gas feed for all the experiments included the following molar concentrations of the species inherent to diesel exhaust: 10% O₂, 8% CO₂, 7% H₂O with the balance of N₂. Depending on the type of experiment, NO_x and/or NH₃ were added to the gas feed in the amount of 200ppm each.

Further details of the experimental setup and the protocols used were previously reported elsewhere [4].

3.0. RESULTS AND DISCUSSION

3.1. IMPACT OF NO OXIDATION ACTIVITY ON SCR PERFORMANCE

<figure 1 here>

As shown in Figure 1, steady-state low-temperature NO_x conversion efficiency of the Cu-zeolite was superior to Fe-zeolite at low NO₂/NO_x ratios. However, with the equimolar mixture of NO and NO₂, both catalysts performed similarly. These results are in good agreement with the earlier literature reports for the catalyst formulations of the same vintage, suggesting that Cu-zeolite was less sensitive to the NO₂/NO_x ratios below 0.5 [3]. Based on the data reported in Figure 1, it would be tempting to ascribe the NO_x performance differences between the two formulations to their different activities in oxidizing NO to NO₂ *in situ*.

In fact, for Fe-zeolite, one could further illustrate the apparent relationship between NO oxidation and NO_x conversion functions using catalyst aging as a probing tool. As shown in Figures 2 and 3, NO oxidation ability and NO conversion at NO₂/NO_x=0 declined concomitantly with aging. NO_x conversion at the optimal NO₂/NO_x ratio of 0.5 was virtually

unaffected by the aging, arguably because *in-situ* NO oxidation is not required.

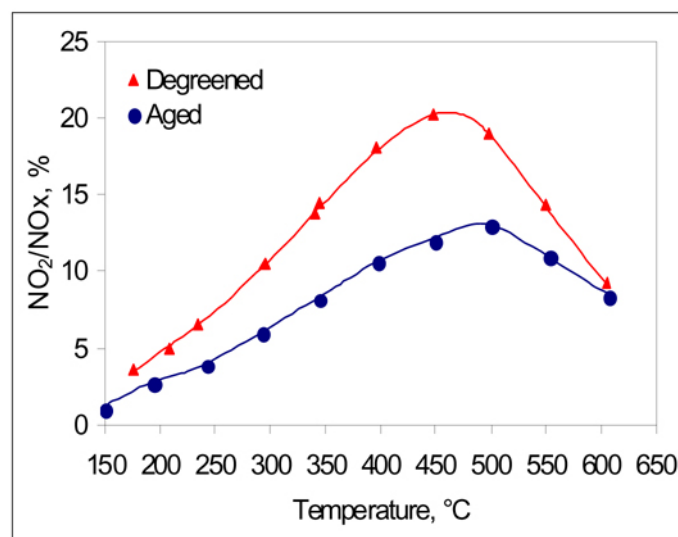


Figure 2. Steady-state NO→NO₂ conversion over Fe-zeolite catalyst, measured in the absence of NH₃

<figure 3 here>

It is worth mentioning here that similar catalyst interrogation approach could not be directly applied to the Cu-zeolite catalyst, due to its superb hydrothermal stability. Virtually no degradation of the NO_x conversion or NO oxidation functions were observed in our testing after aging the catalyst for 100h at 700°C, consistent with the literature reports for Cu-zeolite catalysts of this generation [1,2]. In order to effect catalyst degradation within reasonable time, the temperatures in excess of 800°C are required, possibly resulting in non-representative aging.

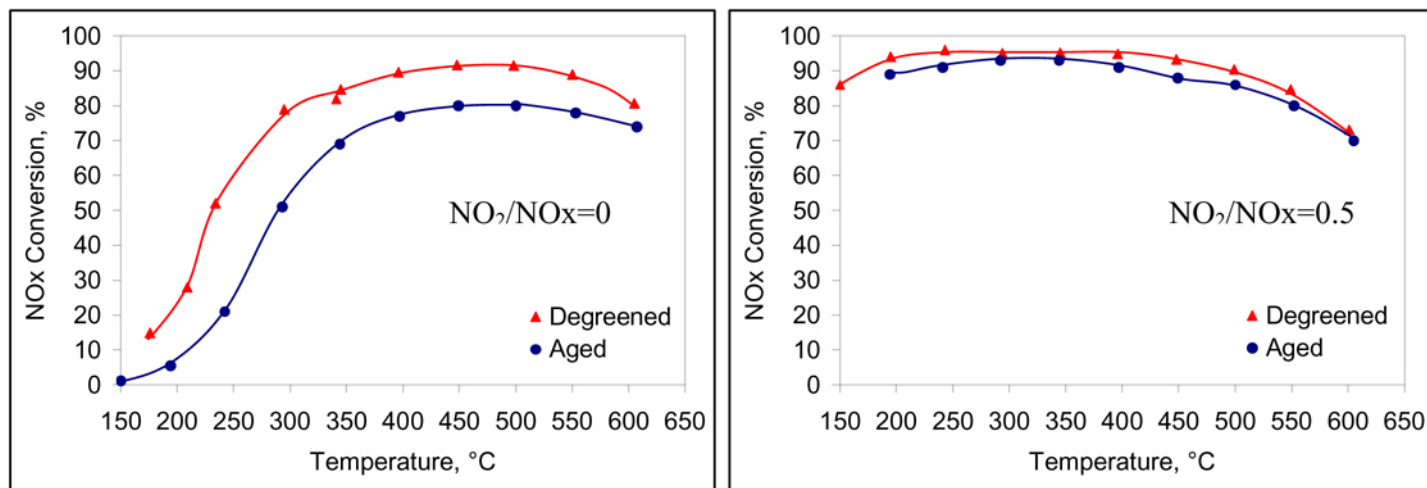


Figure 3. Steady-state NO_x conversion over the degreened and aged Fe-zeolite catalysts at different NO₂/NO_x ratios.

3.1.1. NO Oxidation

In order to verify that the differences between Cu- and Fe-zeolites can be explained due to the differences in their NO oxidation activity, direct measurements of this function were performed. The catalysts were exposed to NO and O₂ in the absence of NH₃ and the resulting conversion of NO to NO₂ is shown by the two solid lines with filled symbols in [Figure 4](#).

Contrary to the expectation that Cu-zeolite is a superior redox catalyst, it was found to be less active than Fe-zeolite in oxidizing NO to NO₂. As a further probe of the redox efficiency of the two catalysts, we have also compared their ability to reduce NO₂ to NO, at conditions where the reverse reaction is thermodynamically favorable. The reverse reaction can provide additional evidence about the redox ability of the two catalysts.

In order to measure the rate of the reverse reaction, the catalysts were exposed to a mixture containing NO₂/NO_x ratio of 0.75. The results are represented by the two dashed lines with empty symbols in [Figure 4](#). Above ~350°C, reduction of NO₂ becomes thermodynamically favorable. The onset of NO₂ reduction for Fe-zeolite occurred at a substantially lower temperature. Overall, Fe-zeolite was clearly more active as a redox catalyst.

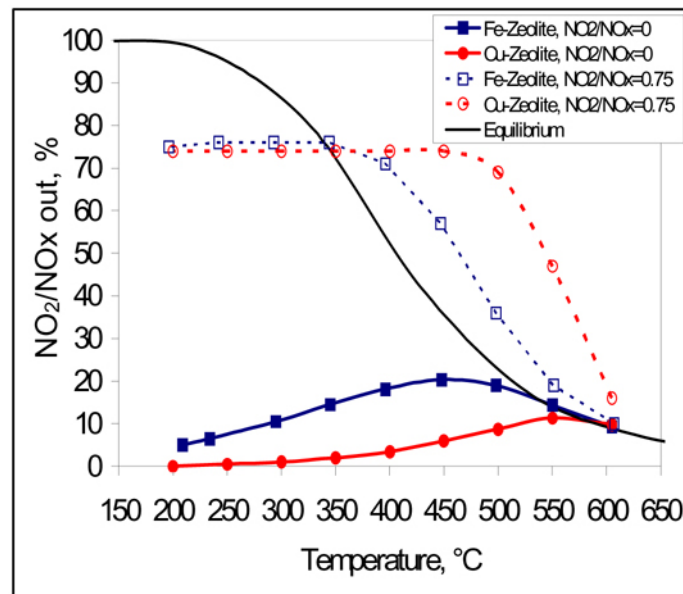


Figure 4. NO oxidation and NO₂ reduction performance of the degreened Cu- and Fe-zeolite catalysts, in the absence of NH₃ in the gas feed.

3.1.2. NO_x Storage

If NO oxidation was indeed the rate-limiting step in the SCR process, one would have to reconcile the apparent contradiction between the Cu-zeolite's excellent low-temperature NO_x conversion at low NO₂/NO_x ratio with its poor NO oxidation performance represented in [Figure 4](#). This would imply that the measurements of NO oxidation in the absence of NH₃ are not applicable for some reason to the SCR conditions. This can only occur if the NO₂ produced is very strongly adsorbed on the surface at low temperatures, thus hindering further oxidation of NO. In contrast, in the