

Combined Fe-Cu SCR Systems with Optimized Ammonia to NOx Ratio for Diesel NOx Control

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ABSTRACT

Selective catalytic reduction (SCR) is a viable option for control of oxides of nitrogen (NOx) from diesel engines. Currently, copper zeolite (Cu-zeolite) SCR catalysts are favored for configurations where the exhaust gas temperature is below 450°C for the majority of operating conditions, while iron zeolite (Fe-zeolite) SCR catalysts are preferred where NOx conversion is needed at temperatures above 450°C. The selection of Cu-zeolite or Fe-zeolite SCR catalysts is based on the different performance characteristics of these two catalyst types. Cu-zeolite catalysts are generally known for having efficient NOx reduction at low temperatures with little or no NO₂, and they tend to selectively oxidize ammonia (NH₃) to N₂ at temperatures above 400°C, leading to poor NOx conversion at elevated temperatures. Fe-zeolite catalysts are very efficient at NOx conversion at temperatures as high as 600°C or higher, but they are not as efficient as Cu-zeolite catalysts at lower temperatures in the absence of NO₂.

In this work, a combined SCR system consisting of an Fe-zeolite catalyst in front of a Cu-zeolite catalyst is tested and compared to a Cu-only system. The experiments are performed on a flow reactor with simulated diesel exhaust gas. It is seen that the operating temperature range of the SCR catalyst can be widened for a combined Fe-Cu system. At low temperatures, the Cu-zeolite improves NOx conversion efficiency vs. an Fe-only system. At elevated temperatures, the Fe-zeolite is more active. Also, one can overdose NH₃ at elevated temperatures with the combined Fe-Cu system without NH₃ slip, while the Fe-only system leads to substantial NH₃ slip when overdosing. A simple optimization of NH₃ to NOx ratio (alpha) is performed for the combined Fe-Cu system and compared to a Cu-only system. Also, the ratio of Fe-zeolite to Cu-zeolite is evaluated. Transient test results are also shown for these systems to determine the impact of a combined system on transient response at low temperatures.

INTRODUCTION

Urea-based selective catalytic reduction (SCR) is an aftertreatment method that has great potential for diesel vehicle applications to help meet Tier 2 Bin 5 emissions requirements [1]. Several recent papers have demonstrated the performance differences between iron zeolite (Fe-zeolite) and copper zeolite (Cu-zeolite) SCR catalysts for NOx reduction from diesel engines (see, e.g. [2, 3]). It has become clear that Cu-zeolite SCR catalysts have improved performance at relatively low temperatures with little or no NO₂ vs. Fe-zeolite SCR catalysts, while Fe-zeolite catalysts have better high temperature performance.

This paper explores the potential improvement of using an aftertreatment system that combines Fe-zeolite and Cu-zeolite SCR catalysts in series in an attempt to take advantage of the desirable characteristics of each. Such a combined system would have an Fe-zeolite catalyst to improve NOx conversion performance at high temperatures and a Cu-zeolite SCR catalyst to improve low temperature SCR catalyst performance and to help oxidize NH₃ at elevated temperatures and high space velocities. These are the conditions where Fe-zeolite SCR catalysts have a risk of NH₃ slip.

This paper reports on experimental results obtained on combined Fe-zeolite + Cu-zeolite SCR systems at different Fe:Cu ratios and compares these results to the performance of a Cu-only catalyst of the same volume, all with varied ammonia:NOx ratio (alpha). The potential benefits of a combined system vs. a Cu-only system are discussed based on the experimental results. The goal of this work is to find an optimal configuration for NOx conversion performance over a broad range of temperatures and space velocities.

EXPERIMENTAL SETUP

Figure 1 gives a schematic of the three configurations analyzed for this paper. The work was done with separate zones of Fe-zeolite and Cu-zeolite catalysts rather than on a homogeneously coated catalyst. In this way, the NH₃ and NOx are exposed to the Fe-zeolite catalyst before passing over the Cu-zeolite catalyst. The

opposite configuration, a Cu-zeolite catalyst in front of an Fe-zeolite catalyst, was not evaluated because it is expected that at elevated temperatures where the Fe-zeolite catalyst would be effective, the Cu-zeolite catalyst would consume the NH_3 before the Fe-zeolite catalyst could make use of it (due to the high NH_3 oxidation potential of Cu-zeolite catalysts at elevated temperatures [2]).

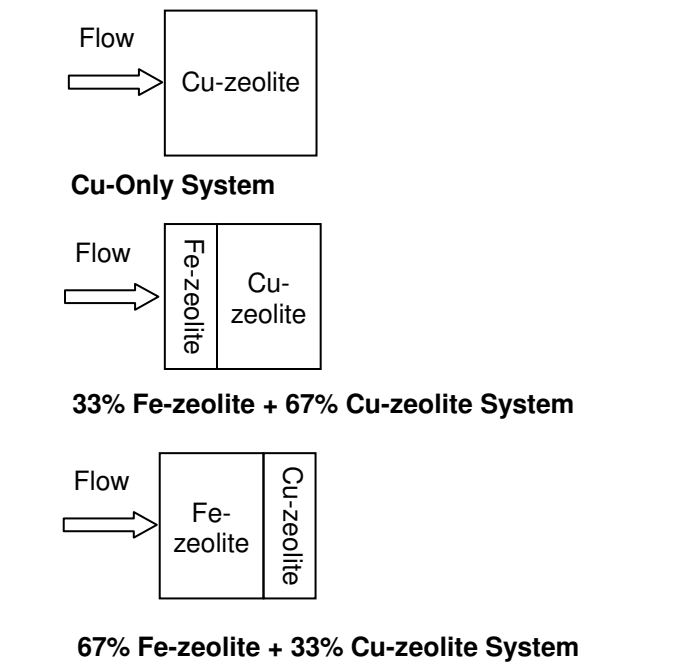


Figure 1: Schematic of the three SCR catalyst system configurations tested for this paper.

As shown in Figure 1, three SCR catalyst configurations were evaluated: 100% Cu-zeolite (Cu-only), 33% Fe-zeolite + 67% Cu-zeolite and 67% Fe-zeolite + 33% Cu-zeolite. Results for an Fe-only system are not shown since the low temperature NO_x conversion performance for the Fe-only catalyst was deemed to be too low relative to the Cu-only or the combined systems. Evaluations were performed at two space velocities, $30,000\text{ h}^{-1}$ and $80,000\text{ h}^{-1}$ at steady state. In addition, transient testing was carried out on initially empty (zero NH_3 storage) catalysts at $80,000\text{ h}^{-1}$.

The catalyst volume and flow rate were changed for the two space velocities. For the $30,000\text{ h}^{-1}$ space velocity, the samples were 1 inch (2.54 cm) in diameter and 1 inch (2.54 cm) in total length with a flow rate of 6.44 L/min. For the $80,000\text{ h}^{-1}$ space velocity evaluations, the samples were 1 inch (2.54 cm) in diameter and 0.625 inch (1.59 cm) in total length with a flow rate of 9.66 L/min.

All tests were performed on washcoated substrates with 400 cells per square inch and 4 mils wall thickness. All samples were hydrothermally aged for 64 hours at 670°C with 14% O_2 , 5% H_2O , 5% CO_2 , balance N_2 at $30,000\text{ h}^{-1}$ space velocity to simulate 120,000 miles of operation in a system with an actively regenerating filter.

Figure 2 shows the flow bench reactor used for these evaluations. The system consisted of quartz tubing and pre-heat tube furnace to ensure a relatively uniform catalyst sample temperature followed by a second tube furnace with the catalyst sample. The NH_3 was injected between the two furnaces to reduce NH_3 oxidation on the tube walls at elevated temperatures. Gas measurements were taken with a Midac FTIR with a heated sample cell.

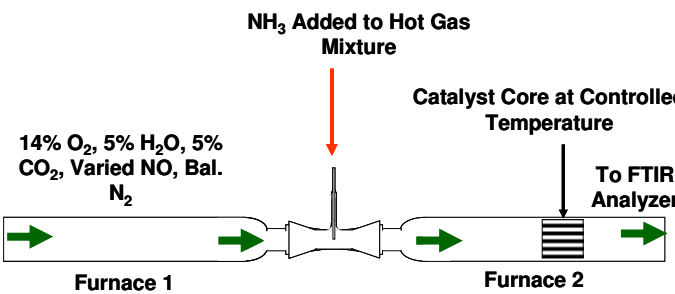


Figure 2: Schematic of flow bench reactor used to characterize catalyst systems.

Table 1 shows the steady state test conditions. The alpha ratio was varied by changing the NH_3 flow rate while keeping the NO flow rate constant. For simplicity, the $\text{NO}:\text{NO}_x$ ratio was 1 for all tests, since this is expected to be a worst case condition for an aged aftertreatment system.

Ammonia gas was used for these laboratory tests due to the complexity of using liquid urea on this small scale. The hydrolysis activity of the two catalyst types (Cu-zeolite and Fe-zeolite) is expected to be similar since the hydrolysis is a strong function of surface area and acidity, both of which are similar for the two catalysts used.

Table 1: Test conditions evaluated for each Fe-zeolite/Cu-zeolite configuration.

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7
NO	350 ppm	350 ppm	350 ppm	350 ppm	350 ppm	350 ppm	350 ppm
NO ₂	0						
NH ₃	245 ppm	315 ppm	350 ppm	385 ppm	420 ppm	525 ppm	700 ppm
Alpha	0.7	0.9	1.0	1.1	1.2	1.5	2.0
O ₂	14%						
H ₂ O	4.5%						
CO ₂	5%						
N ₂	Balance						

RESULTS

PERFORMANCE AT VARIED $\text{NH}_3:\text{NO}_x$ RATIO (ALPHA), 30 k h^{-1} SPACE VELOCITY

The first set of results was obtained from testing at a space velocity of $30,000\text{ h}^{-1}$. Figures 3, 4 and 5 show the NO_x conversion efficiency vs. temperature at varying alpha ratios for the Cu-only system, the 33% Fe-zeolite + 67% Cu-zeolite system and the 67% Fe-zeolite + 33% Cu-zeolite system, consecutively.

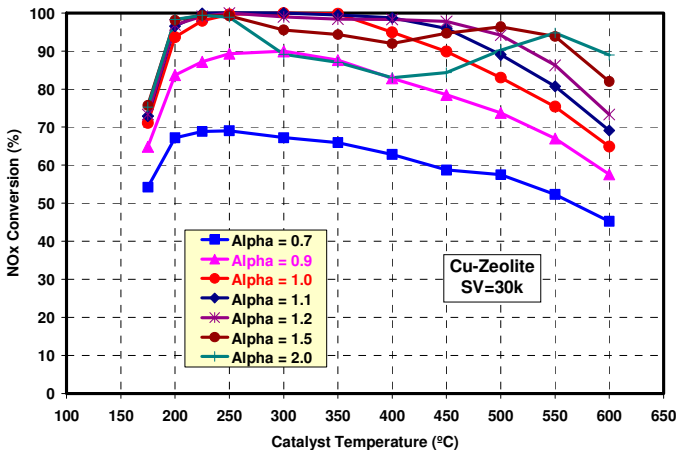


Figure 3: Steady state NO_x conversion efficiency vs. temperature for a Cu-only SCR catalyst at varied alpha ratios.

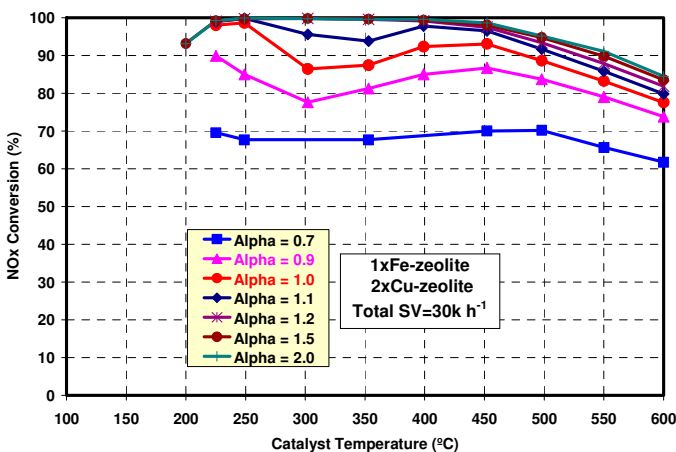


Figure 4: Steady state NO_x conversion efficiency vs. temperature for a SCR catalyst comprised of 33% Fe-zeolite + 67% Cu-zeolite at varied alpha ratios.

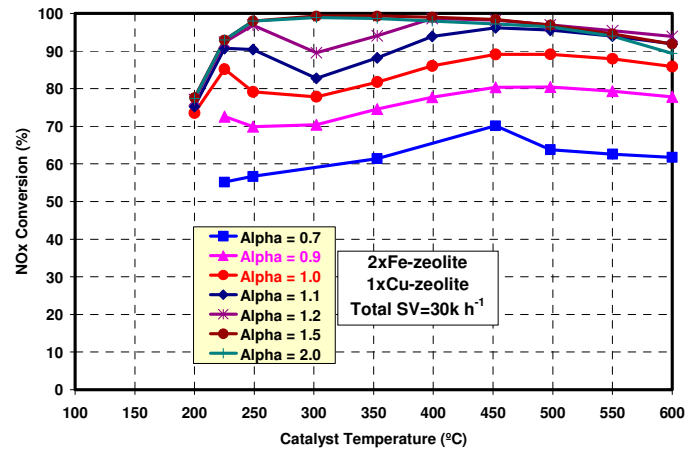


Figure 5: Steady state NO_x conversion efficiency vs. temperature for a SCR catalyst comprised of 67% Fe-zeolite + 33% Cu-zeolite at varied alpha ratios.

For the Cu-only SCR, significant overdosing can have a negative impact on NO_x conversion efficiency in a temperature range from 300 to 500°C (Figure 3). This particular Cu-zeolite SCR catalyst becomes active for NH_3 oxidation ($2\text{NH}_3 + 3/2\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$) at approximately 300°C . It appears that the NH_3 oxidation reaction competes with the SCR reaction for active sites. At temperatures above 500°C , the catalyst appears to be active enough that both reactions can occur.

It can be seen from Figures 4-5 that the systems having some Fe-zeolite catalyst tended to be bi-modal at $\alpha = 1$, with separate peaks in NO_x conversion occurring at 225°C and 500°C . This was believed to be due to the combined effect of the Cu-zeolite and the Fe-zeolite: the Cu-zeolite achieves light-off at lower temperatures, giving high NO_x conversion at 200 and 225°C , while the Fe-zeolite has higher NO_x conversion efficiency at elevated temperatures.

The dip in the NO_x conversion efficiency vs. temperature curves for the combined Fe-zeolite + Cu-zeolite systems was believed to be caused by the higher ammonia consumption of the Fe-zeolite catalyst at moderate temperatures (see results in Cavataio et al. [2]).

PERFORMANCE AT $\alpha = 1$, 30 k h^{-1} SPACE VELOCITY

Figure 6 compares the NO_x performance vs. temperature at $\alpha = 1$ for the three combinations. Here, the bimodal nature of the two systems containing Fe-zeolite was clearer and the potential benefits of the different systems were demonstrated. At this relatively moderate/low space velocity, the system with 33% Fe-zeolite appeared to have a similar light-off temperature to the Cu-only system. The Cu-only system had better performance at temperatures of 450°C and below, but the combination systems had better NO_x conversion performance at temperatures above 450°C .