

Modeling and Performance Analysis of a Field-Aged Fe-Zeolite Catalyst in a Heavy Duty Diesel Engine Application

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ABSTRACT

In this study a 1-dimensional computational model of a Fe-Zeolite catalyst, implementing conservation of mass, species and energy for both gas and catalyst surface phases has been developed to simulate emissions conversion performance. It is applied to both a fresh catalyst and one that has been aged through exposure to the exhaust system of a Heavy Duty Diesel engine performing in the field for 376K miles. Details of the chemical kinetics associated with the various NO_x reduction reactions in the two Fe-Zeolite configurations have been examined and correlated with data from a synthetic gas rig test bench. It was found that the Standard reaction, $(4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O})$, which is one of the main reactions for NO_x reduction, degraded significantly at the lower temperatures for the aged system. Meanwhile the Fast reaction, $(4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O})$, was the least affected and as such became the dominant mechanism for obtaining compliant NO_x reduction levels towards the end of the product's rated life.

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INTRODUCTION

Since 2004, the Environmental Protection Agency (EPA) has mandated a series of restrictions in the levels of NO_x emitted by heavy-duty diesel engines with an aim to achieve a significant reduction of gases considered potentially damaging to the environment. During this period, the allowable limit for NO_x has decreased from 5.3 g/kW·hr to 0.27 g/kW·hr.

Due to their relatively high efficiency, urea based Selective Catalytic Reduction (SCR) exhaust mufflers are currently the leading technology of choice within the Heavy Duty Diesel industry to achieve these NO_x limits. Although these systems are subject to aging related effects, including reduced catalytic activity over time, [1,2,3] regulations require that they be capable of meeting the EPA mandated NO_x levels for the entirety of their rated operational life.

With that in mind, the current study aims to provide insight into the chemical kinetic mechanisms that define the performance and aging process of the system through a combination of fielded system aging and laboratory test bed operation. A synthetic gas rig is employed to characterize the chemical kinetic behavior of individual species reactions within the catalyst, enabling a comparison between a fresh Iron-Zeolite (Fe-Z) based muffler and one that has undergone healthy aging in the field for approximately 376,000 miles, which represents ninety percent of its rated useful life.

As part of this study, a one-dimensional computational model of a Fe-Z catalyst urea SCR after-treatment muffler system has also been developed, which includes the effects of mass diffusion and mass transport, with surface phase reactions of the catalyst considered. This model is used to provide a bridge for comparison of the chemical kinetic data obtained in the lab, and the performance changes experienced in the field aged system.

TESTING AND METHODS

Traditionally, commercial performance testing on a urea SCR muffler containing complete catalyst coated substrates is conducted using a laboratory based test bed (Figure 1), to replicate the fielded system. It includes a Heavy Duty Diesel engine, a diesel particulate filtration system and the catalytic converter hardware. The urea SCR muffler is placed at the end of the system to clean up the NO_x emissions from the engine.

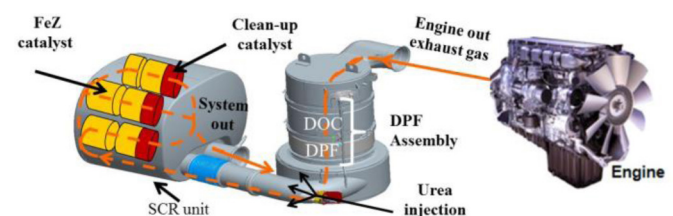


Figure 1. Diagram of Experimental Test Set-up

It must also be noted from Figure 1 that there are two types of catalyst in the urea SCR muffler. One is the Fe-Z catalyst, the main formulation that reduces the NO_x species from the engine exhaust emissions; the other is the Fe-Z+Clean-up catalyst, where this formulation consumes any remaining unreacted NH₃ species so that ammonia is not emitted into the atmosphere as an unintended and unwanted byproduct of the process. The exhaust from the engine typically includes a varying mixture of NO, NO₂, O₂, H₂O and CO₂ with all reactions of interest taking place simultaneously. This makes it impractical to isolate the specific kinetic parameters for each species that define the reactions occurring within the flow for any given set of conditions. Therefore, to study the chemical kinetics in a more controlled fashion, synthetic gas rig testing was employed [4].

A schematic of a synthetic gas rig is depicted in Figure 2. The process involves testing a 1 in. diameter by 3 in. long cylindrical core that is extracted from a full, catalyst coated substrate. The sample is placed in a temperature controlled reactor enclosure. It is then exposed to a regulated mixture of gases, allowing for both preheating and control of moisture content in order to simulate the composition and temperatures of engine exhaust gas. The resulting species exiting the reactor section are then analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to determine species type and amounts, thereby enabling the characterization of separate and specific reactions.

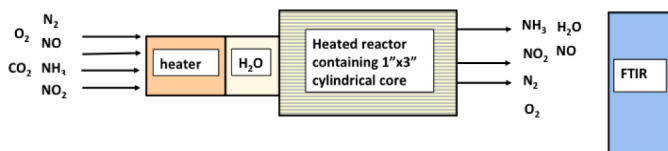


Figure 2. Diagram of Synthetic Gas Rig

Fresh vs. Aged Sample Testing

The same basic approach was applied to testing both fresh and aged samples, though some differences in processes and sample condition were involved either out of necessity or in an effort to improve testing logistical efficiencies.

Typically, the performance of a brand new coated substrate changes significantly during a brief, initial period of operation before the catalytic activity plateaus and remains relatively stable thereafter for the bulk of its operational lifetime. To insure that fresh catalyst under test was performing at levels that are representative of this stabilized condition, the samples first underwent a de-greening process in which they were heated to a company based higher exhaust temperature for a specified timeframe standard to drive the catalytic activity to its stable state, consistent with practices followed when implementing full size catalysts in fielded applications. For obvious reasons, no such de-greening was applied to field aged samples.

To obtain field aged samples, a Heavy Duty Diesel vehicle was subject to special monitoring and operated for 376,519 miles under typical cross-country conditions. During that time it was routinely exposed to exhaust temperatures of approximately 200°C to 400°C. It was also exposed to somewhat higher temperatures of between 350 °C and 500 °C for brief periods (approximately 0.3 percent of the muffler's lifetime), for the purpose of burning off the

accumulated hydrocarbons and soot in the Diesel Particulate Filter. This is a maintenance process known as regeneration that must be performed on all such fielded catalytic systems on an as needed basis. As a result, the field aged Fe-Z catalyst can be analyzed with the knowledge of exposure to what are considered healthy yet realistic operational temperatures.

Some minor procedural differences were adopted between the fresh and aged sample testing which occurred several months apart, in order to manage scarce test bed resources more efficiently. While these differences should not impact the test results, they are noted here for completeness. Care was taken to ensure that testing was initiated with zero NH₃ storage within the sample on all tests. For the fresh samples, this involved testing individual reactions, measured with an MKS Gas 2030 Fourier Transform Infrared Spectroscopy (FTIR), once full NH₃ storage was achieved. For the aged samples this involved conducting the NH₃ storage test first as shown in Figure 3. The species were measured with a Nicolet Thermo Scientific 6700 FTIR, and then two more separate reaction tests were conducted one after another as shown in Figure 7 and Figure 8. Since the steady state values were the intended results, the data was considered valid and the model coefficients for the fresh catalyst were correlated with the fresh testing inputs, and the model coefficients for the aged catalyst were correlated with the aged test inputs. All tests were conducted at system temperatures of 200 °C, 300 °C and 400 °C, with the exception that fresh sample tests were limited to a minimum temperature of 250 °C.

Reaction Specific Procedures

The NO_x reduction reactions considered in this study are shown in Table 1, where each reaction rate constant (r_i) is assumed to follow a version of the basic Arrhenius relationship such that:

$$r_i = k_i e^{\frac{-Ea_i}{RT_{avg}}} \quad (1)$$

The frequency factor (k_i), activation energy (Ea_i) along with the NH₃ storage capacity (Ω) of the catalyst were determined based on the experimental method of Shost et al. [5].

Table 1. Fe-Z NO_x reactions

Reaction	Chemistry	#
NH ₃ Adsorption:	$\text{NH}_3 + \text{NH}_3(\text{S}) \rightarrow \text{NH}_3(\text{S})$	R1
NH ₃ Desorption:	$\text{NH}_3(\text{S}) \rightarrow \text{NH}_3 + \text{NH}_3(\text{S})$	R2
NH ₃ Oxidation:	$4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$	R3
NO Oxidation:	$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	R4
Standard reaction:	$4\text{NH}_3 + 2\text{NO} + 2\text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O}$	R5
Slow reaction:	$8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$	R6
Fast reaction:	$4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$	R7
N ₂ O generation:	$4\text{NH}_3 + 4\text{NO}_2 \rightarrow 2\text{N}_2\text{O} + 2\text{N}_2 + 6\text{H}_2\text{O}$	R8

The NH₃ Adsorption / Desorption test involved injecting 500 ppm NH₃ into an oxygen free simulated exhaust stream, passing it through the pre-conditioned fresh Fe-Z catalyst core and measuring the reduction of NH₃ content at the catalyst outlet. The exhaust consisted of 85% (± 5%) N₂, 7.5% (± 2.5%) H₂O and 7.5% (± 2.5%) CO₂. The minimal variations in the carrier gas are not believed to significantly affect the chemistry coefficient calibrations.

Figure 3 depicts typical NH₃ adsorption/desorption test results. Once the catalyst NH₃ storage is filled and ammonia slip is achieved, the NH₃ slip is allowed to stabilize for some time. Subsequently the reductant injection is cut and desorption of the stored NH₃ from the catalyst takes place. Integrating the difference between the NH₃ injected and the post catalyst NH₃ output measured also yields the calculated NH₃ storage capacity (Ω).

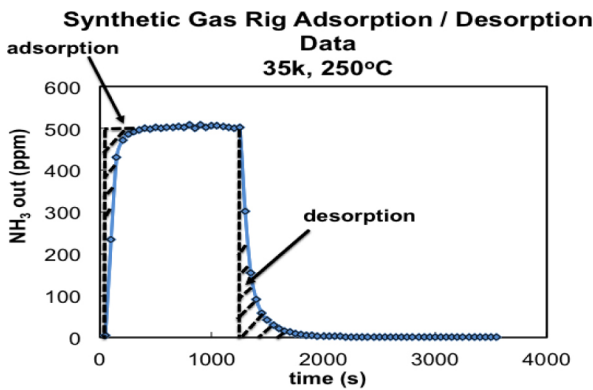


Figure 3. Example of Adsorption, Desorption and NH₃ Storage Test at 250°C

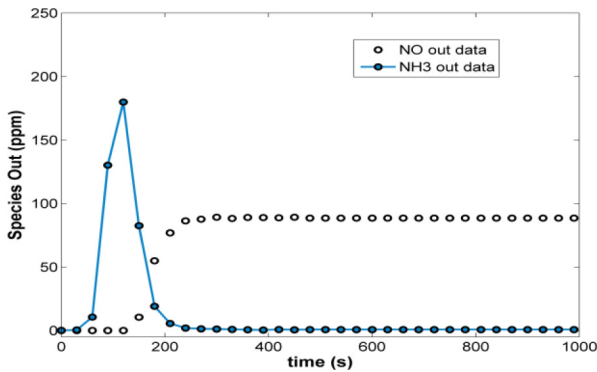


Figure 4. Sample Standard reaction test

To determine NO, NO₂ and NO_x reaction rate constants for the other reactions, tests were conducted with a simulated exhaust gas consisting of 77% (±3%) N₂, 8% (±2%) O₂, 7.5% (±2.5%) H₂O and 7.5% (±2.5%) CO₂. This involved injecting NH₃ into the simulated exhaust flowing into an empty, pre-conditioned catalyst core, and once NH₃ slip was achieved (and thus ensuring that adsorption is complete and NH₃ storage is filled), the appropriate amount of NO, or NO₂ or NO and NO₂ was introduced. The Standard reaction involved 500ppm of NO, the Slow reaction included 375 ppm of NO₂ for the fresh and 375ppm NO₂, 125ppm NO for the aged (~3/4 mole stoichiometric value for NH₃, compared to a mole value of one for

NO) and 250ppm NO and 250ppm NO₂ were the gas feed for the Fast reaction for both fresh and aged catalysts. It must be noted that the N₂O generation reaction and the slow reaction both require the same gas feed, and therefore coefficients from both reactions can be acquired from a single test. The NH₃ Oxidation reaction rate test consisted of injecting 500ppm of NH₃ with a carrier gas containing oxygen. An example of the Standard reaction is shown in Figure 4.

MODELING APPROACH

To simulate the NO_x reducing reactions, the Urea SCR models of Shost et al. [5] and Sukumar et al. [6] have been adopted in part or in whole as the basis for both the Fe-Z catalyst as well as the clean-up catalyst which is described further in this section. Also, for this model it is assumed that the urea delivers complete NH₃ to the catalyst.

The required gas concentrations and associated surface concentrations for the NH₃, NO, NO₂ and N₂O species are determined by equations (2) and (3) respectively such that:

$$\phi \frac{dC_{g,i}}{dt} = -\phi u \frac{(C_{g(z+dz,i)} - C_{g(z,i)})}{dz} K m_i S_v (C_{g,i} - C_{s,i}) \quad (2)$$

$$(1 - \phi) \frac{dC_{s,j}}{dt} = K m_i S_v (C_{g,i} - C_{s,i}) \pm \sum r_i \quad (3)$$

The reaction rates for the various reactions listed in Table 1 are calculated according to equations (4) through (11), which hold for both surface and gas states. Also the temperatures are the post catalyst exhaust gas temperatures, this temperature is believed to demonstrate the overall/average temperature of the catalyst.

$$r_{ads} = k_{ads} e^{\left(\frac{-E_{a_{ads}}}{RT_{avg}}\right)} C_{NH_3} (1 - \theta_{NH_3}) \quad (4)$$

$$r_{des} = k_{des} e^{\left(\frac{-E_{a_{des}}(1 - \alpha \theta_{NH_3})}{RT_{avg}}\right)} \theta_{NH_3} \quad (5)$$

$$r_{NO} = k_{NO} e^{\frac{-E_{a_{NO}}}{RT_{avg}}} \frac{C_{NO}^M C_{O_2} \theta_{NH_3}}{1 + k_{NO} C_{NO} k_{O_2} C_{O_2}} \quad (6)$$

$$r_{NO_2} = k_{NO_2} e^{\frac{-E_{a_{NO_2}}}{RT_{avg}}} C_{NO_2} \theta_{NH_3} \quad (7)$$

$$r_{NO_x} = k_{NO_x} e^{\frac{-E_{a_{NO_x}}}{RT_{avg}}} C_{NO_2} C_{NO} \theta_{NH_3} \quad (8)$$