

Axially Resolved Performance of Cu-Zeolite SCR Catalysts

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ABSTRACT

In this work, an alternative method is proposed and validated for quantifying the axial performance of a state-of-the-art Cu zeolite SCR catalyst. Catalyst cores of a standard length, with varying lengths of wash-coated regions were used to axially resolve the functional performance of the SCR catalyst. This proposed method was validated by quantifying the catalyst entrance and exit effects, as well as the effect of non-uniform wash-coat loading densities. This method is less susceptible to some of the complications highlighted in the previous studies, such as flow uniformity between channels, as well as radiative heating effects, since the product gases are sampled across the entire monolith cross-section rather than through a single catalyst channel. The specific catalyst functions quantified include: NO and NH₃ oxidation, NH₃ storage capacity, as well as NO_x conversion efficiency. The NO_x conversion performance of the catalyst was evaluated for both the standard (NO₂/NO_x=0) and fast (NO₂/NO_x=0.5) SCR reactions as a function of both axial length and catalyst operating temperature.

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INTRODUCTION

NH₃-SCR catalysts have emerged in recent years as one of the key enablers for meeting the stringent environmental regulations for diesel engines and other lean combustion sources [1]. NH₃-SCR catalysts have become the preferred means of meeting the most recent North American and European emission standards for medium and heavy duty on-road trucks. While alternative methods of controlling NO_x from lean burn engines such as NO_x storage reduction (NSR) catalysts are still preferred for many light duty products, the recent adoption of greenhouse gas (GHG) emissions regulations in the United States [3] may force light duty lean burn engines to adopt NH₃-SCR catalysts for NO_x reduction due to the fuel penalty encountered during rich regeneration of NSR type catalysts.

The most recent class of NH₃-SCR catalysts are based on metal-exchanged zeolites, especially Cu- and Fe-based. The overall performance of this new class of zeolites has been well documented [3], and substantial improvements have been made to these catalysts in a rather short period of time [4], which has led to the successful deployment of zeolite based catalysts around the globe as the preferred means of

NO_x reduction. In particular, it has been reported that Cu-zeolite SCR catalysts require high levels of stored NH₃ in order to effectively reduce NO_x emissions [5]. This characteristic of operation emphasizes the importance of a fundamental understanding of the functional performance of these catalysts in order to effectively control reductant delivery to optimize NO_x conversion efficiency. Further increasing our understanding of these catalysts by axially resolving the functional performance of NH₃-SCR catalysts may help develop improved reductant delivery control strategies. In order to appropriately size SCR aftertreatment elements, and to create superior reductant delivery control strategies, it is imperative to gain a full understanding of the axially resolved functional performance of these catalysts.

Multiple studies [6-7] have documented the use of Spatially Resolved Capillary Mass Spectrometry (Spaci-MS) for quantifying the performance of diesel oxidation catalysts (DOC). However, the use of this technique for axially resolving the performance NH₃-SCR catalysts has not been described in literature at the time of this publication due to the difficulties of quantifying NH₃ concentration in the presence of H₂O via conventional mass-spectrometry. One technique that was successfully employed was Spatially

Resolved Capillary Fourier Transform Infrared Spectroscopy (Spaci-FTIR) [8]. While this technique was capable of axially resolving the performance inside a single channel of the catalyst monolith, a dilution feed was required in order to achieve satisfactory transient resolution due to the rather large FTIR cell. Furthermore, the authors found that probing a single channel of catalyst monolith was inherently sensitive to heterogeneous aging of the catalyst core in a radiative furnace.

In this work, we have proposed and evaluated an alternative method for axially resolving the performance of NH_3 -SCR catalysts by creating catalyst cores with varied lengths of catalyst wash-coat. A conventional way of comparing the impact of catalyst length on its performance would have entailed using catalyst cores of different length, fully coated with the catalyst. However, changing the length of the core confounds the effect of the catalyst amount as such with potential fluid mechanical complications, related to the channel entrance and exit effects. This becomes increasingly concerning, as the sample length decreases. In contrast, in this work we have decoupled the fluid dynamics from the catalyst length as such, by using sample cores of the same size, with catalyst zones of different length and located at either inlet or outlet side of the core.

EXPERIMENTAL METHODS

CATALYST MATERIALS

Cylindrical samples 25.4mm (1in) in diameter by 152.4mm (6in) in length were cut from a cordierite monolith substrate with 62 cells per cm^2 (400 cells per in^2). This substrate was 6in in length, and was coated with a state-of-the-art Cu-zeolite formulation on the first 76.2mm (3in). The other 76.2mm of the substrate were left uncoated, which allowed the catalyst cores to be cut such that the coated length of the test core could be varied from 12.7mm (0.5in) to 76.2mm. The catalyst samples were provided by Johnson Matthey, Inc. Multiple 76.2mm (3in) long catalyst cores with coated lengths varying from 12.7mm to 63.5mm were used for this study. Prior to each test, each core was degreened at 700°C for 1hr in a gas feed containing 10% O_2 , 8% H_2O , 7% CO_2 , and a balance of N_2 to complete the catalyst preparation process.

BENCH REACTOR SYSTEM

A simplified schematic of the reactor system used for all experiments is shown in Figure 1. The reactor system consists of a 38mm (1.5in) OD $\times$ 32mm (1.25in) ID quartz (fused silica) tube. The reactor tube was installed into a Lindberg three-zone electric furnace. Quartz pre-heater tubes of 2mm ID $\times$ 4mm OD were placed inside of the quartz reactor tube in order to improve heat transfer to the feed gas, as well as to ensure even flow distribution at the inlet of the catalyst core. The 25.4mm diameter catalyst cores were placed inside the reactor tube approximately 75 mm downstream of the quartz

preheater tubes. The catalyst core was held in place via frictional normal forces by using an Interam mat which was compressed between the core and the quartz reactor tube. Three Omega Type K thermocouples were installed in the catalyst core in order to record gas inlet, catalyst inlet, and catalyst outlet temperatures. The gas inlet thermocouple was located approximately 5mm upstream of the inlet face of the core, while the catalyst inlet and outlet thermocouples were imbedded in the core approximately 3mm from the inlet and outlet faces of the core, respectively.

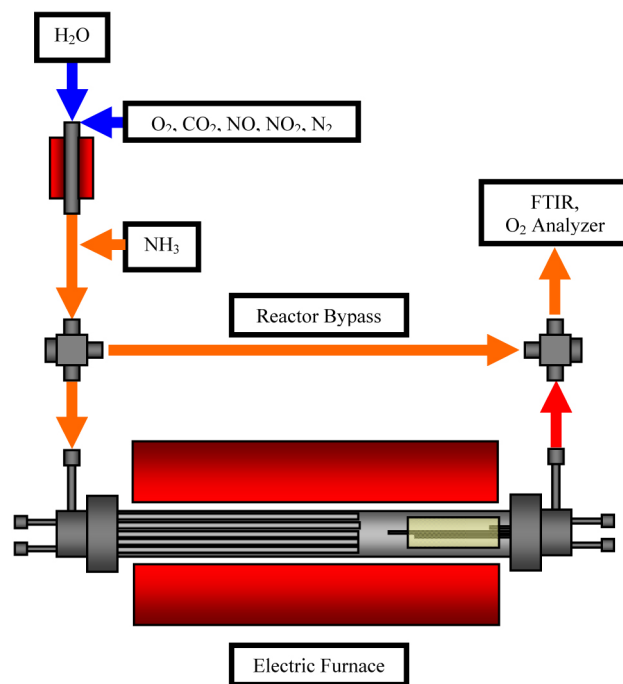


Figure 1. Representative schematic of bench reactor system

Zero air was generated in the laboratory using a Peak Scientific zero air generator. All other reacting gases were of research grade and supplied by AirGas. All gases were metered by MKS mass flow controllers calibrated for their respective gas species and flow range requirements. Unless otherwise noted in the text, all tests were carried out with a GHSV of $40,000\text{hr}^{-1}$. Liquid water was injected into a custom heated vaporizer via a pair of computer controlled ISCO 10000D syringe pumps. Pneumatically actuated high-temperature 3-way valves were located both upstream and downstream of the quartz reactor section to enable bypass of the reactor system for reactant feed gas sampling. All reactor inlet lines were heated to 165°C to prevent condensation or adsorption of any reactant species, including NH_3 . The outlet of the reactor system was connected to an MKS 2030 Series FTIR for species quantification. A needle valve and vacuum pump were connected to the outlet of the FTIR in order to maintain a constant 10slpm flow rate through the FTIR. Excess reactor exhaust not sampled through the FTIR was either sampled by the CAI 600 series paramagnetic O_2

analyzer, or vented. All reactor outlet lines were heated to 195°C to prevent condensation or adsorption of any product species.

EXPERIMENTAL METHODOLOGY

Multiple test protocols were utilized in order to complete the study documented here, consisting of two distinct components:

- The first part of the study was a catalyst geometric study, which was developed to quantify the effect of fluid mechanics, namely entrance and exit effects on catalyst cores with very short regions of catalyst wash-coat in order to validate our methodology for the axially resolved measurements.
- The second component of this study was the characterization of catalyst performance as a function of axial length. In this portion of the study, multiple catalyst functions were analyzed and quantified as a function of axial length.

Detailed descriptions of the two fundamental catalyst studies completed during this study are provided below in further detail.

The four-step protocol developed by Kamasamudram et al. [1], and schematically shown in Figure 2, was used to quantify various catalyst functions. The functions probed by this protocol included NO oxidation, NH₃ oxidation, NOx conversion, NH₃ storage, and NH₃ slip. It was applied for both the standard (NO₂/NOx=0) and fast (NO₂/NOx=0.5) SCR reactions and at multiple catalyst temperatures to ensure the axially resolved behavior was fully captured in all of the practically-significant operating regimes, as follows. A catalyst temperature of 200°C was selected as the low-temperature point where the standard SCR reaction is relatively slow and requires very high levels of NH₃ storage in order to reach maximum NOx conversion efficiency. At this low temperature, the standard SCR NOx conversion of the catalyst is thought to be limited predominantly by the amount of NH₃ stored on the catalyst. Catalyst temperatures of 350°C and 400°C were chosen as moderate temperatures where the standard SCR reaction is very fast, NH₃ storage capacity is relatively low, and parasitic NH₃ oxidation is still relatively slow. Finally, a catalyst temperature of 550°C was chosen as the high-temperature operating point where NH₃ oxidation is no longer insignificant, and begins to negatively impact the overall NOx conversion performance of the catalyst. These four temperatures well encompass the major operating regimes of the Cu zeolite SCR catalyst, and can provide insights into the axially resolved performance of the SCR catalyst in these operating regimes.

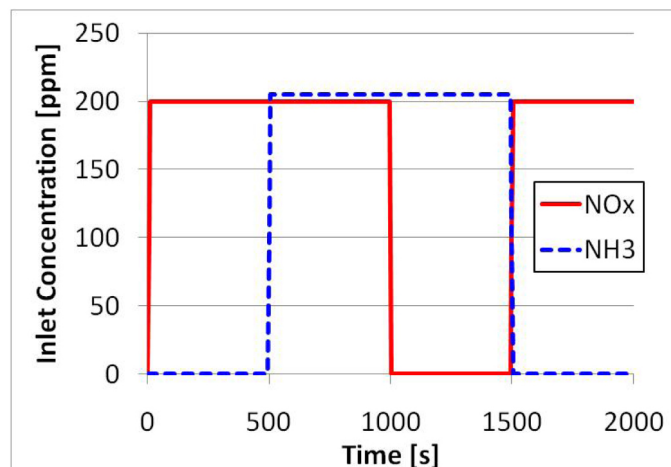


Figure 2. Four-step protocol, used to quantify the functional performance of the SCR catalyst cores.

Catalyst Geometric Study

The methodology proposed in this text for quantifying the catalyst performance as a function of axial length consists of utilizing 76.2mm catalyst cores with various lengths of applied catalyst wash-coat. One point of concern with this proposed method was the effect of entrance and exit flow on catalyst performance. As discussed in the Introduction, we used cores of different total length and different length of catalyzed zone on them, in order to quantify the potential impact of the fluid mechanics factors on the overall performance. Specifically, a 152.4mm long catalyst core was removed from the half wash-coated brick. 63.5mm was removed from the coated side of the core, and 12.7mm was removed from the uncoated side of the core. The resulting 76.2mm catalyst core consisted of 12.7mm of wash-coated substrate, and 63.5mm of uncoated substrate. This core will be referred to as the “long core”. A second catalyst core was used to quantify the effect of shortened core length on catalyst performance. This catalyst was fully coated and 12.7mm in length. This core will be referred to as the “short core”. Thus, in both cases the total amount of catalyst material should be identical (12.7mm catalyzed zone in both cases), while the total length of the cores varied between 12.7mm to 76.2mm for the “short” and “long” cores, respectively.

Furthermore, in order to evaluate the effect of core entrance and exit effects on catalyst performance, the long catalyst core was tested in two ways. In the first experiment, the wash-coated region was placed upstream, at the sample inlet. In the second experiment, the core orientation was reversed, such that the wash-coated region was placed downstream, at the catalyst outlet. The results were compared to the short core. Since these cores were cut from different parent cores, wash-coat loading density can have a substantial impact on the functional performance of these cores. In order to isolate the effect of total catalyst length from variations in