

Cu-Zeolite SCR Catalyst Thermal Deactivation Studied with FTIR Spatial Resolution

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ABSTRACT

The performance of a commercial Cu-zeolite SCR catalyst after differing degrees of hydrothermal aging (aged for 72 hours at 500, 700 and 800°C with 10% moisture balanced with air) was studied by spatially resolving different key reactions using gas-phase FTIR measurements. Gases were sampled along a channel at different positions and analyzed using FTIR, which overcomes the interference of water and nitrogen on ammonia concentration detection encountered in standard mass spectrometer-based spatial resolution measurements. The NO:NO₂ concentration ratio was changed so that the standard (NO:NO₂ = 1:0), fast (NO:NO₂=1:1) and NO₂ (NO:NO₂ = 0:1) SCR reactions could be investigated as a function of the catalyst's hydrothermal aging extent. In addition, the effects of hydrothermal aging on the activity of NH₃ and NO oxidation were also investigated.

Hydrothermal aging had little effect on NO oxidation activity. For standard and fast SCR processes, NO_x conversion attained its maximum at 300°C. Hydrothermal aging decreased reaction rates for SCR and NH₃ overconsumption simultaneously. However, selectivity to NH₃ overconsumption was high over the highly aged catalyst at high temperatures. NO was oxidized to NO₂ at the outlet portion of the catalyst under standard SCR conditions at high temperatures, suggesting a balance between NO oxidation and SCR at limited NH₃ concentrations. NO conversion under standard SCR conditions decreased more with hydrothermal aging compared to NO_x conversion under fast SCR conditions. Coincidentally, NH₃ overconsumption was more significant under standard SCR versus fast SCR conditions.

Along a monolithic catalyst channel, the extent of reaction changed with the NO:NO₂ composition. When both NO and

NO₂ were present in the inlet gas, the fast SCR reaction dominated. At temperatures below 200°C, a small amount of reaction between NH₃ and NO₂ was also observed. Standard SCR became more significant with NO₂ depletion along the catalyst. However, the fast SCR reaction at high temperatures can be limited by the decomposition of NO₂ at the front of the catalyst.

Hydrothermal aging decreased the extent of NO₂ decomposition into NO at high temperatures, which helps maintain fast SCR reaction conditions in the system. The effects of hydrothermal aging on NH₃ oxidation was more complicated. Generally, aging reduced NH₃ oxidation activity, but it did not change monotonically with aging extent and neither did NO_x produced via NH₃ oxidation. However, the highly aged catalyst did produce a high proportion of NO_x.

INTRODUCTION

Selective catalytic reduction (SCR) systems are being implemented to meet mandated emission standards, which are becoming more stringent globally, with Euro VI and US Tier Bin5 regulations as examples [1]. Typically, the SCR catalyst is part of a multi-component aftertreatment system, located behind a diesel oxidation catalyst (DOC) and before or after a diesel particulate filter (DPF). Cu/zeolite formulations are being evaluated due to their ability to achieve high NO_x conversion at the lower operating temperatures typical of diesel engine exhaust. One of the current concerns for zeolite-based catalysts is their ability to maintain performance after an exposure to high temperature in the presence of moisture. During its lifetime, the SCR catalyst will encounter severe hydrothermal aging conditions when the diesel particulate filter is regenerated, with trapped soot beginning oxidation at ~550°C, with higher temperatures encountered downstream

due to the exothermic nature of carbon oxidation [2, 3]. In addition, an emerging technology being developed involves depositing the SCR catalyst onto the conventional wall-flow particulate filter [4]. The potential for over-temperature events during soot regeneration on this aftertreatment device may require SCR catalyst durability at temperatures as high as 800 to 900°C for short periods of time.

SCR catalyst deactivation has been studied by many researchers [3, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Generally speaking, catalysts can be deactivated chemically, thermally, and mechanically. In this study, the focus is on the effect of hydrothermal aging on catalyst performance. Two SCR hydrothermal aging deactivation mechanisms have been proposed: dealumination and sintering. In terms of steam-induced dealumination, the lattice aluminum migrates, resulting in structural degradation of the zeolite and therefore a loss in activity. For example, Pieterse et al [12] found that deactivation of zeolite-based cobalt and palladium catalysts are in part caused by temperature-induced ion migration. Grinsted et al [13] proposed that dealumination leads to a loss of Brønsted acid sites. The authors observed that the activity decreased rapidly upon catalyst exposure to 410°C in wet air, but no loss in activity was observed with dry air exposure. The copper content of the catalyst impacts resistance to dealumination [13, 14, 15]. The introduction of the Cu²⁺ before steaming preserves these sites from total destruction although some morphology change may still occur. According to Kuchеров et al [15], when both Cu²⁺ and Al³⁺ ions are present in the zeolite framework, the structure is more flexible and is therefore less prone to structural changes. Sintering is a process involving migration of active particles, the particles coalescing, and therefore overall component particle growth. Karas et al [16] proposed that the thermal deactivation of Cu-ZSM-5 is mainly due to copper sintering. The authors found that even a brief period of catalyst operation at 600-800°C resulted in substantial deactivation and significant losses in micro-pore volume. As the temperature was increased, a substantial portion of the copper was sintered to CuO, or perhaps Cu₂O, accompanied by a loss in zeolite crystallinity. The authors also proposed that CuO crystallites grow primarily within the zeolite pores. As these crystallites exceed critical sizes, the local zeolite structure is destroyed, which caused the observed loss in micro-pore volume. Their conclusions were supported by the work done by Park et al [14], who found that Cu ions migrated within the zeolite structure during aging processes.

The ability to spatially resolve reactions is becoming more common as a catalyst testing method for researchers to study reaction mechanisms, as such methods provide more information than integral (inlet and outlet), steady-state measurements and are therefore quite useful in developing and validating models [17, 18]. Spatially resolved gas-phase concentrations along lean NO_x trap (LNT) catalysts, to investigate activity changes with exposure to sulfur, have been obtained by researchers at Oak Ridge National Laboratory [19]. These studies showed different

activity regions inside the LNT catalyst and how they change as a function of sulfur poisoning. This Spatially Resolved Capillary Inlet Mass Spectrometry (SpaciMS) technique [18, 20] has also been used to monitor competitive reactions along a DOC and apparent NO oxidation inhibition in the presence of hydrocarbons [21]. Spatially-resolved gas-phase concentrations as well as temperatures at the catalyst surface have been measured during C₃H₆ oxidation before and after homogeneous and heterogeneous thermal degradation [17, 22]. Such spatial profiles show where and how quickly different species are formed or consumed along the catalyst axis. Evaluating the relative reaction extents under different conditions also determines the extent of catalyst use and can help optimize the catalyst length and volume. Furthermore, such data can be used to develop significantly more robust models of catalyst performance. To date, spatial resolution has been primarily accomplished with mass spectrometry [17, 18, 21, 22, 23, 24, 25, 26].

In this paper, the performance and hydrothermal durability of a Cu/zeolite based SCR catalyst are studied by spatially resolving gas concentrations along the catalyst using a Fourier-Transform Infra-Red (FTIR) analyzer. FTIR was used in order to avoid the complication of NH₃ measurements using a mass spectrometer in the presence of significant amounts of H₂O and N₂. The results clearly demonstrate where the different reactions occur along the catalyst as well as their reaction rates under different steady-state test conditions, with insight into the effect of deactivation on their rates clarified.

EXPERIMENTAL

CATALYST

The catalyst for this study was supplied by BASF Corporation. The catalyst is a Cu exchanged chabazite containing 3.5 % copper expressed as copper metal, with a nominal silica to alumina ratio (molar) of 35:1. The exchanged zeolite was coated on 400 cells per square inch cordierite ceramic honeycombs, dried and then calcined at 450 °C for 30 minutes. The copper exchange and coating followed steps described in US patent 7,490,464 [27]. The samples used for these tests were cut from a full-size monolith, and were 2.0 cm long and 1.6 cm in diameter. The catalysts were de-greened in ambient air at 750°C for 4 hours and then hydrothermally aged at three different conditions.

HYDROTHERMAL AGING

The samples were aged in a reactor for 72 hours at 500, 700 and 800°C. The reactor consists of a horizontal quartz tube reactor, heated by an Applied Test Systems, Inc. Series 3210 temperature-controlled electric furnace. Hollow quartz tubes were located upstream of the catalyst sample to improve heat transfer. During aging, the inlet and outlet catalyst temperatures were monitored by Omega K-type thermocouples located in the middle of the reactor tube approximately 1 mm upstream and downstream of

the catalyst sample. The catalyst sample was wrapped with heat-expanding insulation material supplied by DBW GmbH & Co. and placed inside the heated zone of the furnace in an approximately isothermal position, such that the inlet and outlet temperatures varied by less than 10°C. The total flow rate during aging was 6.0 liters/min. The gas composition consisted of air and 10% H₂O. These three samples, aged at 500, 700 and 800°C, are described throughout the paper as lightly aged (L), medially aged (M) and highly aged (H), respectively.

REACTOR SET-UP

The hydrothermally aged catalyst samples were wrapped with heat-expanding insulation material and inserted into a horizontal quartz tube reactor, which was heated by a Lindberg temperature-controlled electric furnace. A schematic of the reactor set-up is shown in [Figure 1](#). Temperatures at the front and back of the catalyst were monitored using Omega K-type thermocouples. The catalyst was located in an approximately isothermal position within the furnace, with average catalyst temperatures reported in this work.

To sample the gases along the channel of the monolith, a fused silica capillary was inserted into the desired cell. The capillary size was 0.68 mm OD, and 0.53 mm ID. The sampling point was positioned conveniently by pulling or pushing the capillary through a 4-layer septum at the reactor outlet. The capillary outlet was connected to a tee where dilution nitrogen (180 ml/min) was mixed with the sampled gas. A Thermo Scientific Nicolet 6700 FTIR analyzer was used to measure NO, NO₂, N₂O, NH₃, H₂O and CO₂ concentrations. The sampled gas amount through the capillary was controlled to about 20 ml/min by slightly adjusting the pressure within the reactor. The average flow in each cell was 47 ml/min. The reactor pressure was kept relatively constant, between 960 and 990 Torr. Keeping the diluting N₂ flow rate and CO₂ inlet concentration constant, the measured FTIR CO₂ concentration could be used to calculate and monitor the sampled amount of gases through the capillary. Also, the CO₂ concentration were kept the same when moving the capillary through the monolith, which demonstrates the flow rate through the channel being sampled did not change either.

All the gases were supplied by Airgas, except N₂, which was supplied by Praxair. The gas flows were controlled with Tylan and MKS mass flow controllers. Upstream lines were heated and maintained at 170°C to vaporize water and prevent it from condensing. Water was added via a Masterflex 7523-60 pump into the upstream tubing, where it was vaporized. To avoid the formation of ammonium nitrate between NO₂ and NH₃ on any upstream components, the latter was introduced directly at the inlet of the reactor. For all SCR reactions, the simulated exhaust gas contained 400 ppm of NO_x (NO+NO₂), 400 ppm NH₃, 10% O₂, 5% H₂O, 7% CO₂ and balance N₂, and the total gas flow rate was 4.8 L/min, corresponding to a gas hourly space velocity (GHSV) of 48,000h⁻¹. For NH₃ oxidation tests, the NH₃ inlet concentration was 360 ppm, while O₂, H₂O and CO₂ were the same as above, and the GHSV was 48,000 h⁻¹. For NO oxidation, the NO inlet concentration was 200 ppm, while O₂, H₂O and CO₂ levels were the same as above, and the GHSV was 30,000 h⁻¹. For NH₃ adsorption, the NH₃ inlet concentration was 200 ppm, while O₂, H₂O and CO₂ were the same as above, and the GHSV was 30,000 h⁻¹. The quantity of adsorbed NH₃ was measured through NO titration after the catalyst was saturated.

RESULTS AND DISCUSSION

For the convenience of discussion, the experiments where just the outlet concentrations were measured, i.e. not through the capillary, but by directing the whole flow through the FTIR analyzer, are labeled as a normal test. For all key reactions, both spatially-resolved and normal tests were conducted and their results were compared to check the reliability of the spatial resolution technique by monitoring and evaluating any differences between the two techniques. For all the comparisons between spatially-resolved and normal tests, the data from spatial resolution tests were collected at 1.8 cm from catalyst front, with the catalyst being 2.0 cm long as mentioned above. Unless otherwise specified, the channels tested were located in the middle (radially) of the monolith. Standard SCR, fast SCR, and SCR with different NO to NO₂ ratios, and NH₃ and NO oxidation were spatially resolved for all three aged catalyst samples.

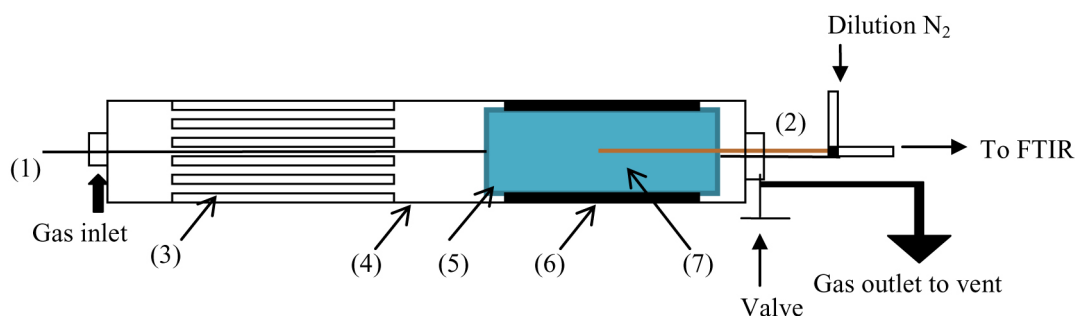


Figure 1. SCR reactor and spatial resolution sampling unit: (1) inlet thermocouple, (2) outlet thermocouple, (3) hollow quartz tubes, (4) quartz reactor tube, (5) catalyst monolith, (6) insulation/wrapping material, (7) silica capillary.

NORMAL VERSUS SPATIALLY RESOLVED RESULTS - RADIAL AGING DISTRIBUTION IN MONOLITH CORE SAMPLES

For the lightly and medially aged catalysts, the standard SCR and fast SCR reaction performances, including the conversion of NO_x and NH_3 , and NH_3 oxidation results, obtained either via the spatial resolution technique when measuring at 1.8 cm or through the normal method, were approximately the same. As an example, the NO conversion results as a function of temperature obtained during the two types of tests for the

medially aged catalyst are shown in Figure 2(a). From these data it is apparent that there is not much difference between the results obtained by the two methods in testing this sample, demonstrating that the spatial resolution test technique is reliable. However, for the highly deactivated catalyst, the spatially-resolved NO_x and NH_3 conversions observed during standard SCR, fast SCR, and NH_3 oxidation reaction tests were higher than those obtained during the normal tests, with the NO conversion as a function of temperature during standard SCR as an example, shown in Figure 2(b). The differences between the spatially-resolved and normal test results, the latter of which is the average of all the results from each channel, indicate that the activities of different channels in the monolith must vary.

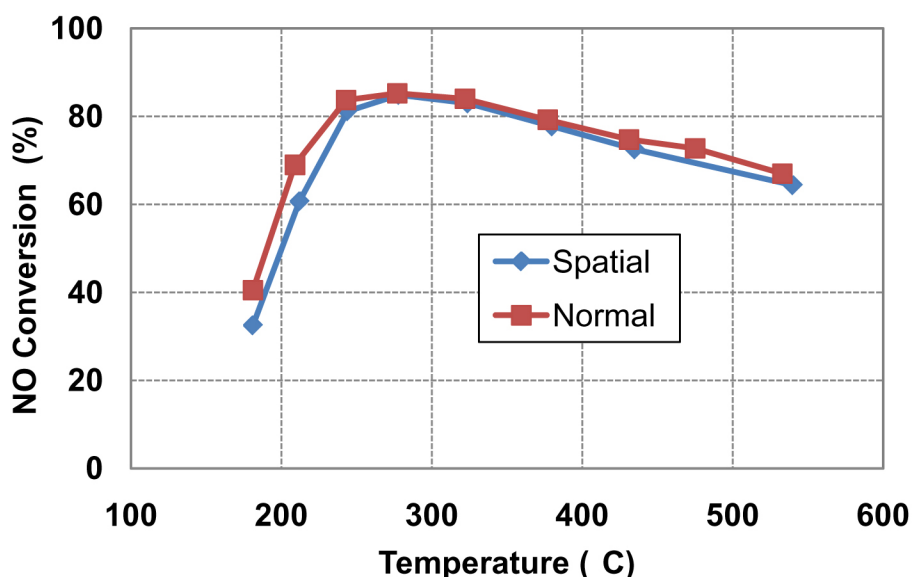


Figure 2(a). Standard SCR NO conversion comparison between normal and spatially-resolved tests for the medially aged catalyst. $\text{GHSV} = 48,000 \text{ h}^{-1}$, inlet concentrations $\text{NO} = 400 \text{ ppm}$, $\text{O}_2 = 10\%$, $\text{H}_2\text{O} = 5\%$, $\text{CO}_2 = 7\%$.

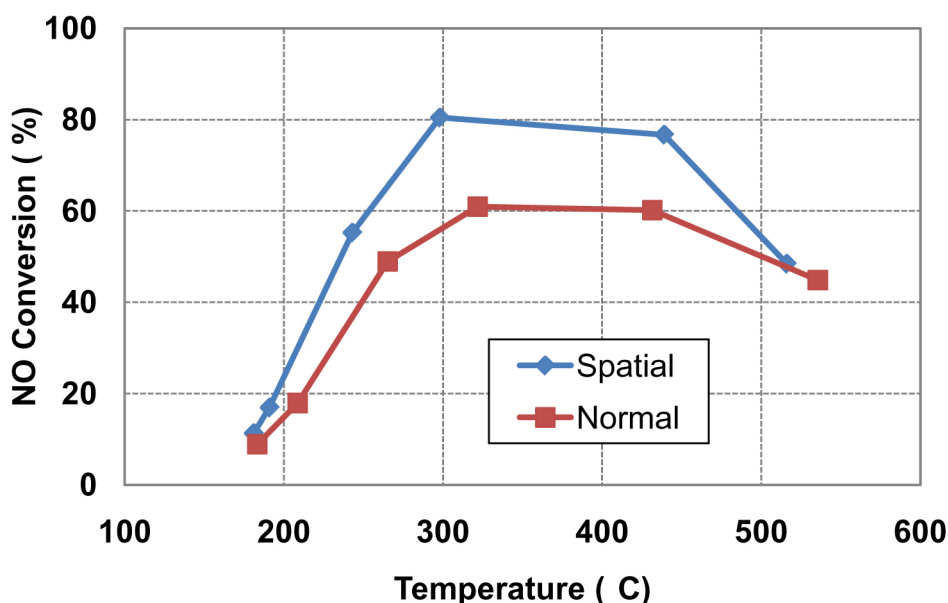


Figure 2(b). Standard SCR NO conversion comparison between normal and spatially-resolved tests for the highly aged catalyst. $\text{GHSV} = 48,000 \text{ h}^{-1}$, inlet concentrations $\text{NO} = 400 \text{ ppm}$, $\text{O}_2 = 10\%$, $\text{H}_2\text{O} = 5\%$, $\text{CO}_2 = 7\%$.

Based on the above results, the homogeneity of catalyst aging was evaluated for the three aged catalyst samples. Standard SCR, fast SCR and ammonia oxidation in channels at different radial positions of the monolith were monitored using the spatial resolution technique. The results, which are not shown here, indicated that for the lightly and medially aged catalysts, there was no significant difference in activity for channels located at different radial positions of the monolith. However, for the highly aged catalyst, activity differences were observed at different radial channel positions. For channels near the center of the monolith, the reaction activity was higher for standard and fast SCR relative to channels located near the

edge of the monolith, as shown in Figure 3 for data obtained at 250°C, where No. 1 refers to the first channel from the edge, and No. 6 refers to the sixth channel from the edge, which is located in the center of the monolith. For standard SCR, the NO conversion in channel 6 is 2.5 times higher than the conversion in channel 1, while the conversion difference between channel 1 and 6 for the fast SCR reaction is not as significant. The reason for the smaller difference associated with the fast SCR reaction will be explained below. Corresponding to the NO_x conversions in the standard and fast SCR reactions, NH₃ conversions between the channels followed similar trends (data not shown).

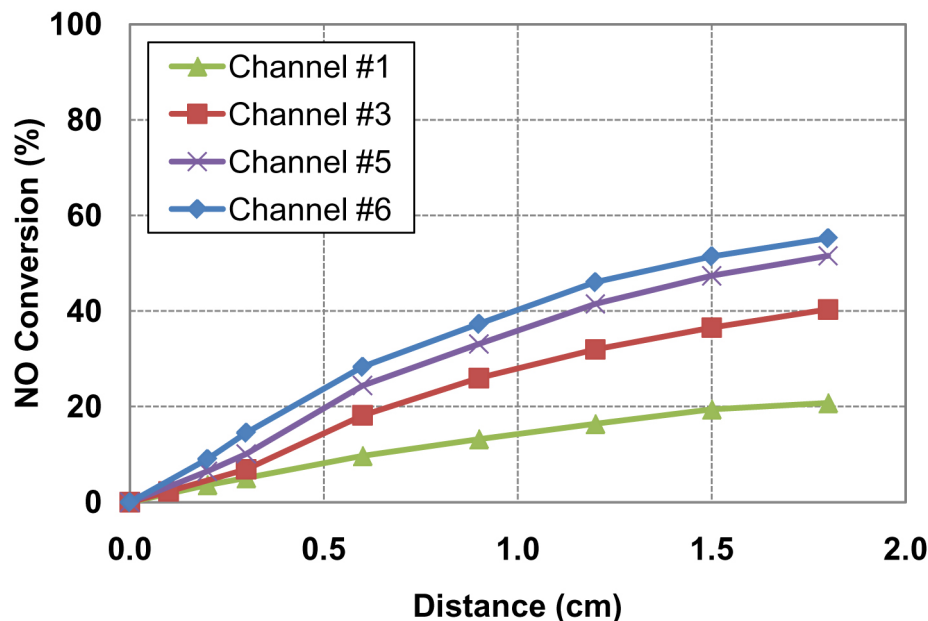


Figure 3(a). Standard SCR NO conversions at 250 °C in channels located at different radial positions in the highly aged catalyst. GHSV= 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

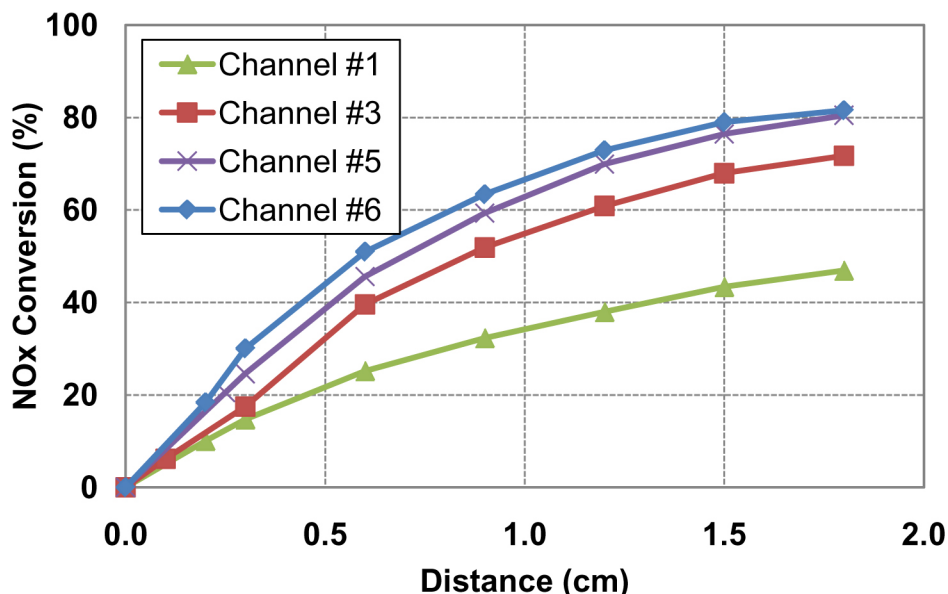


Figure 3(b). Fast SCR NO_x conversions at 250 °C in channels located at different radial positions in the highly aged catalyst. GHSV= 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 200 ppm, NO₂ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

There were significant differences in the XRD patterns (results not shown) obtained between the samples aged at 700 and 800°C. Based on these results, and the experimental set-up, where the control thermocouple is at the radial center of the catalyst, the outer edges must experience more severe aging during the nominally 800°C hydrothermal aging treatment. Significant radial gradients must not have existed for the lightly and medially aged samples or were not large enough to induce changes in the catalyst. When the samples were aged at 800°C, the temperature difference between the center and edge of the monolith was approximately 20°C, and this gradient caused the large differences in activity noted. Consistent with the literature [3, 16], these data suggest that the copper zeolite structure collapsed between 700-800°C, and any excursion above 800°C could induce further damage. Hydrothermal aging below 700°C did not induce such a change and therefore the activity in all channels was approximately the same. When the catalyst sample was aged around the critical temperature where the zeolite structure will collapse, the 10 to 20°C temperature difference along the catalyst radial direction led to the significant activity differences observed.

Based on this evidence, the differences between the results of the spatially-resolved and normal tests for the highly deactivated catalyst are likely due to the heterogeneity in deactivation resulting from the temperature difference along the radial direction during the 800°C hydrothermal deactivation process. The channels in the middle of the monolith are more active than those located elsewhere. Therefore, the NO conversion in this channel was higher than the total conversion over the monolith. There are larger deviations between the tests in the middle temperature range versus those at the extremes, at 180 and 550°C, as shown in Figure 2(b).

The reason for the small difference at low temperature is that NO oxidation is the controlling step for standard SCR at low temperatures [28, 29]. As thermal deactivation has little effect on NO oxidation (as will be discussed below), it causes little difference in the outcome of the standard SCR reaction. At high temperature, NO conversion is limited by the availability of NH_3 . As NH_3 overconsumption is high at high temperature regardless of the degree of deactivation, NO conversions end up being similar at high temperature between the two tests.

IMPACT OF HYDROTHERMAL AGING ON NO OXIDATION

NO oxidation as a function of temperature and catalyst aging was evaluated, with the normal test data shown in Figure 4. The maximum conversion is less than 15% for all three catalysts. The effect of aging on NO oxidation activity was not significant, especially at temperatures below 300°C. One possible reason for the insensitivity of NO oxidation activity to hydrothermal aging extent is that the NO oxidation turnover frequency (TOF) might be structure sensitive [30] over copper compounds. NO_2 TPD results from the aged catalysts (data not shown here) demonstrate that although hydrothermal aging does not significantly influence NO oxidation, it does reduce the number of active NO_x adsorption sites, indicating that copper ions in the zeolite structure either coalesced, and/or maybe merged into copper oxides. Literature evidence shows that as the Cu-zeolite catalyst is aged by exposure to high temperature with moisture, copper ions in the structure migrate and merge into copper oxide particles [16]. If the turnover frequency of NO oxidation over copper oxide particles is higher than that over copper ions in the zeolite structure, the total effect of hydrothermal aging on NO oxidation will not be significant.

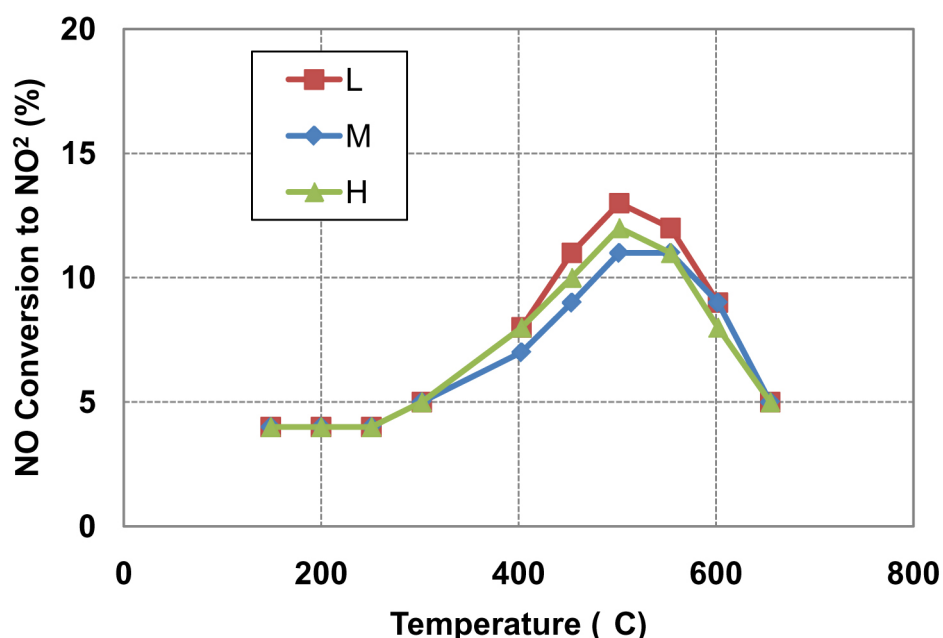


Figure 4. Effect of aging on NO oxidation by O_2 to NO_2 as a function of temperature during a normal test. $\text{GHSV} = 30,000 \text{ h}^{-1}$, inlet concentrations $\text{NO} = 200 \text{ ppm}$, $\text{O}_2 = 10\%$, $\text{H}_2\text{O} = 5\%$, $\text{CO}_2 = 7\%$.

SPATIALLY-RESOLVED STANDARD SCR REACTION

Temperature Effect on Concentration/Conversion Profiles

The effect of temperature on the reactant concentration profiles for the standard SCR reaction as a function of catalyst length was investigated on the three differently aged catalyst samples. As an example of the results, Figure 5 shows the change in NH_3 and NO conversions along the catalyst length as a function of temperature for the lightly aged catalyst. As shown in Figure 5(a), the NH_3 conversion increased monotonically with temperature and catalyst length. Figure 5(b) shows that the NO conversion increased with temperature up to 300°C , where the maximum NO conversion was reached. Although the overall NO conversions were lower at higher temperatures, in the front part of the catalyst NO conversion increased monotonically with temperature. Based on these data, the higher the temperature, the faster the reaction is in the front part of the catalyst, and the distance from the front of the

catalyst that NO conversion begins to slow shortens. The high temperature phenomena are caused by NH_3 overconsumption limiting NO conversion.

In terms of spatially resolved results, another phenomenon noted is increasing NO_2 production at high temperature occurring in the outlet portion of the catalyst as a function of NH_3 loss. As an example, data obtained from the lightly aged catalyst are shown in Figure 6. At the inlet of the catalyst, there are several ppm of NO_2 noted, due to the fact that a very small fraction of the NO was oxidized via reaction with O_2 prior to the catalyst inlet. The NO_2 concentration dropped along the catalyst length due to the fast SCR reaction. However, as the NH_3 concentration decreased to around 50 ppm, NO_2 concentration increased indicating NO oxidation was occurring to enough of an extent to be observed although the fast SCR reaction must also be simultaneously occurring. As the temperature was increased, NO_2 production began earlier although the concentration of NH_3 was still quite high, suggesting a balance between NO oxidation and SCR at limited NH_3 concentrations.

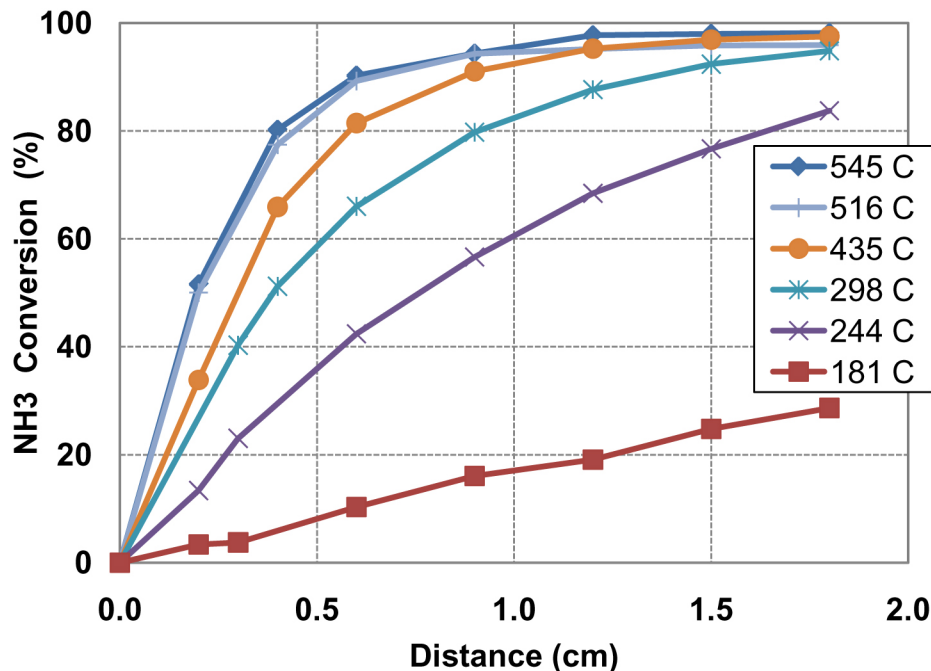


Figure 5(a). NH_3 conversion as a function of catalyst length and temperature when testing the lightly aged catalyst $\text{GHSV} = 48,000 \text{ h}^{-1}$, inlet concentrations $\text{NH}_3 = 400 \text{ ppm}$, $\text{NO} = 400 \text{ ppm}$, $\text{O}_2 = 10\%$, $\text{H}_2\text{O} = 5\%$, $\text{CO}_2 = 7\%$.