

Development of Spatially-Resolved FTIR – Gas Concentration Measurements inside a Monolith-Supported Selective Catalytic Reduction Catalyst

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

The diesel engine is growing in popularity due to its energy efficiency and solving the emissions issues associated with diesel engine exhaust would clear the way for further growth. The key pollutants are NO_x, particulate matter and unburned hydrocarbons. Selective catalytic reduction (SCR) catalysis is likely the best choice for NO_x control. In SCR, NH₃ selectively reacts with NO_x to form N₂ – the selectivity refers to NH₃ reacting with NO_x instead of the abundant O₂. Urea is used as the NH₃ source, being injected into the exhaust as an aqueous solution where the urea decomposes and NH₃ is generated.

Spatial resolution characterization techniques have been gaining attention in the catalysis field because of the higher level of information provided. In this thesis, a new spatial resolution technique, called SpaciFTIR (spatially-resolved, capillary-inlet Fourier transform infra-red spectroscopy), was developed, which overcomes the interference of water in the detection of NH₃ in an earlier developed technique, SpaciMS (spatially-resolved, capillary-inlet mass spectrometry). With the new test method, three SCR topics were addressed.

First, the three key SCR reactions were spatially resolved. These are the standard SCR reaction ($2\text{NO} + 2\text{NH}_3 + 1/2\text{O}_2 = 2\text{N}_2 + 3\text{H}_2\text{O}$), the fast SCR reaction ($\text{NO} + \text{NO}_2 + 2\text{NH}_3 = 2\text{N}_2 + 3\text{H}_2\text{O}$), and NO₂-SCR, ($6\text{NO}_2 + 8\text{NH}_3 = 7\text{N}_2 + 12\text{H}_2\text{O}$). Results show that in the presence of NO₂, but at a NO₂/NO_x ratio < 0.5, the fast SCR reaction proceeds followed by the standard SCR reaction, i.e. in series. If the NO₂/NO_x ratio exceeds 0.5, the NO₂-SCR and fast SCR reactions occur in parallel. Compared to the standard integral test method, this spatial resolution technique clearly showed such trends. Secondly, the spatial resolution technique was used to characterize the effects of thermal aging on catalyst performance. It was found that for a highly aged catalyst, there was a radial activity profile due to an inhomogeneous temperature distribution in the process of aging. Aging effects on various key SCR reactions, i.e. NO oxidation, NH₃ oxidation, and the reduction reactions, were studied. Last but not least, for the purpose of passive SCR system development, transient NH₃ storage profiles along the monolith channel were measured with SpaciFTIR. Passive SCR is a system where the NH₃ is generated on an upstream catalyst, such as a three-way catalyst or lean-NO_x trap, instead of via urea injection. In such a system, NH₃ is therefore not constantly being fed to the SCR catalyst, but “arrives” in pulses. Factors such temperature, NH₃ concentration, pulsing time, flow rate and thermal aging were investigated. For the first time, NH₃ migration was observed and its effect on SCR reactions along the length of catalyst was studied.

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Dedication

I would like to dedicate this thesis to my family, in particular my wife, my daughter, my mother, and my sister, who have been very supportive of my interests and efforts. I believe my strength comes from them.

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Chapter 1: Introduction

1.1 The control of air pollution

Air pollution is a constant concern and developing solutions to eliminate air pollution or slow its increase is a significant challenge. As early as 1306 [1], under the order of Edward I of England, craftsman's furnaces were not allowed to use sea coal because of the fumes produced. But with society's growing awareness of pollution effects, air pollution control has developed from an aesthetic issue to a recognized need.

After the Great Smog of London in 1952 and many other significantly public environment issues, governments around the world started to take air pollution control more seriously. The USA enacted the Air Pollution Control Act [1] in 1955 to strengthen the regulation of air pollution, set numerical limits on the concentrations of a basic group of air pollutants and provide reporting and enforcement mechanisms. Following such initiatives, mandating air pollution control is common to most of the world's governments. More than several hundred chemicals and substances have been listed as pollutants. Nitrogen oxides are one of the most important pollutants we have to deal with in terms of air pollution. How to reduce and eliminate nitrogen oxides in diesel engine automobile exhaust is the focus of this thesis.

1.2 NO_x pollution

NO_x typically refers to a mixture of NO and NO₂, though several other nitrogen oxides exist. They are produced by combustion engines and industrial processes, which are usually categorized into two groups: stationary and mobile. The stationary sources include power plants, nitric acid factories and natural gas turbines. The mobile sources include trucks, cars and any other vehicles. Mixtures of NO, NO₂ and N₂O contribute to different atmospheric pollution phenomena. NO and NO₂ are involved in photochemical smog and acid rain phenomena. While NO is non-toxic by itself at low concentrations, at ground level it contributes to the formation of ozone [2]. Nitrogen dioxide is a reddish brown, highly reactive, toxic gas. Once it has formed, NO₂ can react with other pollutants, such as volatile organic compounds to form a complex HC-NO_x-O_x, which is generally called photochemical smog [3]. At low concentration levels, N₂O is a non-toxic substance. However, it is a well-known greenhouse gas and is also involved in stratospheric ozone destruction [4]. It is expected to be regulated shortly.

1.3 Control of NO_x from automobiles

Automobiles are a significant contributor of NO_x pollutants, with the NO_x originating from the reaction between N₂ and O₂ during the high temperature combustion process. NO_x emissions reduction from automobiles depends on the type of engine. The two most commonly used engines in automobiles are gasoline and diesel engines.

Up to now, NO_x control from gasoline engine emissions has been mainly accomplished using a three-way catalyst (TWC), with which hydrocarbons, CO and NO_x are oxidized and reduced. Thanks to its high energy efficiency, the diesel engine is becoming more common. In order to reduce NO_x emissions from diesel engine exhaust, various techniques have been used, which can be classified as combustion control and post-combustion abatement technologies. The challenge is reducing NO_x in an oxidizing environment. An example of NO_x emissions being reduced through combustion control technologies is exhaust gas recirculation (EGR), which reduces the temperature in the engine cylinders and thereby reduces the amount of NO_x produced. NO_x formation can also be reduced by improving the homogeneity of the fuel/air mixture through techniques such as homogeneous charge compression ignition (HCCI). The main purpose of post-combustion abatement is to reduce NO_x catalytically, for example via catalytic reduction. The focus of this thesis is selective catalytic reduction (SCR) of NO_x in diesel engine exhaust. The reductant is NH₃, which can be added into the system or produced over an upstream TWC or Lean NO_x Trap (LNT).

1.4 Selective catalytic reduction (SCR)

Diesel engines produce exhaust containing a large excess of O₂, so NO_x reduction to N₂ in the O₂-rich exhaust demands a catalyst that can reduce NO_x selectively. The SCR process is based on the selective reaction between NO_x and NH₃, which is injected into the exhaust gas stream, to produce water and nitrogen. To date, zeolite-based catalysts, base metal oxides and catalysts with noble metal components have been found effective for NO_x reduction in the presence of excess O₂. Ag/Al₂O₃ is effective for the SCR of NO_x by hydrocarbons, in particular with C₂H₅OH [5]. NH₃ is very effective for NO_x reduction over Fe- and Cu-zeolites [6-7]. SCR of NO_x by NH₃ has become a fairly mature technology for stationary applications using vanadium-based catalysts [8]. For mobile applications, such as diesel trucks and some lean-burn gasoline cars, commercialization is occurring, as discussed in the following section. Note, gaseous NH₃ is not used in practice for vehicle exhaust NO_x control. Instead, urea solutions are injected into the exhaust, and the urea decomposes to NH₃ and CO₂.

1.5 The application of SCR on vehicles

The application of SCR of NO_x using NH₃ (or urea as an NH₃ precursor) started with marine engines [9]. The early SCR units were installed in carriers [10] and ferries [11], as well as locomotive diesel engines [12].

Since the early 1990s, numerous SCR development projects have been funded by governments [13, 14] and engine companies [15-16]. Catalyst suppliers are of course also contributing to the development of SCR systems. For example, Johnson Matthey has been developing the Compact SCR-Trap system, a device consisting of a particulate filter upstream of an SCR catalyst [17]. Not surprisingly, companies

with traditional expertise in stationary installations also developed mobile systems, such as that of Haldor Topsøe [18].

SCR has been combined with other techniques, such as the lean NO_x trap (LNT) [19-21], where the SCR catalyst is placed downstream to make use of the NH₃ produced on the LNT catalyst.

Mercedes-Benz launched a concept E 250 BlueTec vehicle that uses a urea-SCR system to meet the 2009 US EPA emission standards. Another example is the BMW X5d SUV and 335d Sedan, introduced in 2009 with “BluePerformance” technology, where a urea-SCR catalyst is placed behind a particulate filter to reduce NO_x. Most predictions indicate SCR will become typical for diesel engine exhaust gas clean-up, and may even move into the lean-burn gasoline markets in the future.

Early studies showed that when NO_x is reduced over TWCs and LNT catalysts, NH₃ could be formed. [22-28] Based on such findings, the concept of passive NH₃ SCR was recently proposed [29], where NH₃ is produced during fuel-rich operation, via reduction of the NO_x over the TWC, or LNT. The produced NH₃ is then stored on the downstream SCR catalyst, and can be used as the reductant to reduce NO_x during subsequent fuel-lean operation.

1.6 Research objectives

The diesel engine is growing in popularity due to its energy efficiency. Solving the emissions issues associated with diesel engine exhaust would clear the way for further growth. SCR is likely the best choice for NO_x control.

The goals of the project include:

- Understanding the basic performance of the catalyst.
- Evaluating the effect of catalyst deactivation on performance, including the effect of deactivation on NH₃ storage and oxidation, NO oxidation, and finally on general performance.
- Evaluating NH₃ adsorption in a passive NH₃ SCR system, including how the adsorbed distribution is affected by temperature, time and concentration, and how SCR reactions are affected by the NH₃ adsorption process, together with the effect of thermal aging.

These key elements will define the main factors that affect the activity of SCR catalysts.

1.7 Contents of the thesis

In the following chapters, literature regarding NH₃ SCR systems is reviewed in Chapter 2, including the development of the catalyst system, the reaction mechanisms, SCR catalyst deactivation, and the development of spatial resolution techniques. The experiment setup is described in Chapter 3, and the types of experiments are listed. In Chapter 4, a novel spatial resolution technique with FTIR, SpaciFTIR, is described. In Chapter 5, the results obtained where SpaciFTIR was employed to study the effect of thermal aging on SCR reactions are presented and discussed. NH₃ pulsing adsorption in a passive NH₃

SCR system was investigated, with the results in Chapter 6. The process of NH_3 migration after pulsing adsorption was also monitored.

Chapter 2 Literature Review

2.1 Development of SCR DeNO_x system for diesel engine automobiles

Due to stringent regulations, as well as the small space available on vehicles, the SCR catalyst must be highly efficient. The systems that have been studied, and deemed applicable due to their high efficiencies, can be classified into three groups: those based on noble metals, such as platinum, those based on highly dispersed base metal oxides, and those based on zeolites.

The noble metal group consists primarily of systems based on Pt/Al₂O₃, which have shown significant activity, with the temperature window for NO_x conversion in relatively low temperature ranges [30]. They have, however, the disadvantage of producing relatively high amounts of byproduct N₂O [31] at low temperature and an enhanced activity toward NH₃ oxidation [32-33] at high temperatures, which make them less selective. Besides, the high cost of this kind of catalyst is an obvious disadvantage.

The vanadium-based catalyst is an example from the transition metal oxides class. It is widely used in NO_x control from stationary sources [34-35]. A typical example formulation is V₂O₅/WO₃-TiO₂. The last family of SCR catalysts is the zeolite-based catalysts. Various transition metals have been studied as active components in zeolite-based catalysts.

Zeolite-based systems are the focus of this thesis project. However, a brief review will be given for vanadium-based catalysts, because they have been widely used in stationary facilities and the knowledge gained from this system will benefit the study of the targeted system.

2.1.1 Vanadium-based catalysts

The vanadium-based SCR catalyst has been widely commercialized in stationary facilities, such as for nitric acid plants and for exhaust clean-up of natural gas turbines. Vanadia is responsible for the NO_x reduction activity [36]. The main drawback of this catalyst is that it is easily poisoned by SO₂. Furthermore, at high temperatures, the catalyst is active in the oxidation of SO₂ to SO₃, which results in a rapid decrease in SCR activity and selectivity. Finally, vanadia will sublime above 650°C [37-38], and vanadia is poisonous and could therefore present a new pollution problem. In stationary applications, these temperatures however are not approached.

Usually, TiO₂ is chosen as the vanadia support because TiO₂-based industrial catalysts are only partially, and reversibly, sulfated in the presence of SO₂, and under certain conditions the S exposure can even enhance the SCR catalytic activity [39]. Another advantage of using TiO₂ is that on the anatase phase of TiO₂, vanadium oxide can be well dispersed, giving rise to “isolated” vanadyl centers, which are more reactive [40-41]. MoO₃ and WO₃ are usually added both as stabilizers and as promoters [35] to vanadia-based SCR catalysts and possibly as SO₂ oxidation inhibitors. Because of the toxicity and volatility of the vanadia species, vanadia-based catalysts have not been widely considered applicable for automobile exhaust. Therefore, Fe- and Cu-zeolites were developed to replace vanadium-based catalysts. Some of the

SCR reaction mechanisms on vanadia-based catalysts have been adopted by some researchers to investigate those on zeolite based catalysts, which will be reviewed below.

2.1.2 Zeolite-based catalysts

Cu-ZSM-5 was first studied for NO_x reduction in lean-burn combustion exhaust gas over two decades ago [42-43]. Since then, significant research and development has been dedicated to transition metal zeolites for SCR of NO_x with various reducing agents, such as NH₃ and hydrocarbons. The most popular transition metals supported on zeolites studied for SCR were copper, cobalt, palladium, rhodium, iron, silver, cerium, gallium, indium and manganese [3]. Copper and iron zeolites were found to be of particular significance.

Various zeolites have been proposed for the SCR catalyst support, including ZSM-5, mordenite, zeolite beta, ferrierite, Y-zeolite [3], SAPO [44] and SSZ (chabazite, CHA) [45-47]. In the most active systems, zeolites generally are promoted by transition metals, such as iron, copper, and silver. Judged against vanadium-based SCR catalysts, zeolite-based catalysts are advantageous as they are non-volatile in exhaust gas temperature ranges and can retain catalytic activity after periods at high temperature in the presence of H₂O and SO₂ [48]. However, under harsh hydrothermal conditions, such as at temperatures higher than 500°C, the activity of many metal-promoted zeolites begins to decline, which is believed to be due to destabilization of the zeolite, such as by dealumination and consequent reduction of metal containing catalytic sites within the zeolite. To meet the requirement of high SCR activity at low temperatures and strong hydrothermal durability at high temperatures, up to at least about 650°C, Cu/chabazite (CHA) zeolite catalysts were developed [45], and are of smaller-pore molecular sieve types [47, 49-50]. The CuCHA catalysts have a ratio of silica to alumina from about 15:1 to about 256:1 and a copper to alumina ratio from about 0.25:1 to 1:1. Compared with other zeolite-based catalysts, CuCHA has higher SCR activity at low temperature, higher selectivity to N₂, in particular low N₂O formation, better thermal durability and is relatively resistant to hydrocarbon inhibition [46]. For example, Kwak et al [51] reported that Cu²⁺ ion-exchanged SSZ-13 (Cu-SSZ-13), a zeolite with the chabazite structure and containing small radius (~3.8 Å) eight-membered ring pores, is more active and selective in reducing NO with NH₃ compared to Cu-ZSM-5 and Cu-beta. Fickel et al found that SSZ-13, SSZ-16 and SAPO-34 are more hydrothermally stable than the medium-pore Cu-ZSM-5 and maintain their high SCR activity even after being steamed for periods of up to 15 hours [47]. Cu chabazite SCR catalysts are now considered the industry standard.

2.2 Basic SCR reactions

There are three SCR reactions described in the literature depending on the NO_x source, the standard SCR reaction when there is just NO, the fast SCR reaction when there is both NO and NO₂, and SCR with NO₂ only:



A large fraction of the NO_x in diesel exhaust is composed of NO [52-53]. However, it is found that when the NO₂ fraction is increased to about 50% of the total NO_x, the second reaction listed above occurs, and it is more rapid than the first. Therefore, a catalyst's ability to modify the NO₂/NO_x ratio in situ may have a substantial impact on its performance and it is of interest to study the NO oxidation mechanism over SCR catalysts:



Zeolites can adsorb large amounts of NH₃ and the characteristics of NH₃ storage and release play an important role in determining the transient performance of SCR catalysts. Finally, the oxidation of NH₃ may cause a decrease in NO_x conversion, with oxidation reactions listed as follows:



Obviously, those reactions are not desirable for the SCR system because they consume NH₃ reductant. Cavataio et al proposed that the undesired NH₃ oxidation reactions might also include [53]:



As a part of the evaluation of SCR catalyst performance, it is always necessary to investigate NH₃ oxidation.

Overall, a typical SCR catalyst needs to fulfill several functions. To guide the design and development of an SCR system, understanding the function-specific processes are needed. In the literature, an experimental protocol comprised of four steps has been described, and often adopted, to elucidate those catalytic functions efficiently [54-55]. This method was based on the realization that much higher NH₃ storage on Fe- and Cu-zeolite catalysts makes transient control difficult [54]. The four segments allow steady-state and dynamic functions to be studied. For example, the effect of NH₃ coverage on NO_x conversion under different driving modes was investigated. Using coverage-dependent NO_x conversions, instead of the typical steady-state conversion maps, leads to a more accurate representation of the catalyst capabilities under a real-world driving circle.

Regarding SCR kinetics, many research groups have devoted significant effort to obtaining kinetic rate expressions, with the following section reviewing the findings according to the specific reaction.

2.3 SCR reaction mechanism

For the SCR reaction system using NH_3 as the reducing agent, the mechanism of NH_3 adsorption and activation, standard SCR and fast SCR reactions have been studied. Together with those topics, studies on the role of NO_2 , NH_3 oxidation and NO oxidation are also reviewed below.

2.3.1 NH_3 adsorption and activation

Regarding NH_3 adsorption, how it is adsorbed, the active intermediates, and how it is oxidized on the catalyst surface need to be understood. It is generally agreed that NH_3 can be adsorbed on both Lewis and Brønsted acid sites. When it is adsorbed through a Lewis-type interaction, it takes the form of molecularly adsorbed NH_3 while over Brønsted acidic surface hydroxyl groups, ammonium ions are formed. Both types of acidic sites have been proposed as the active centers [56]. Lietti et al [57] found, however, that when NH_3 is protonated as a NH_4^+ ion over Brønsted sites, it is thermally less stable than the molecularly coordinated species. Takagi et al. [58] and Miyamoto et al. [59] suggested that the active NH_3 species over vanadia-based catalysts are NH_4^+ ions, so activation of NH_3 would occur on the catalyst surface Brønsted acid sites. Several other authors supported a key role of Brønsted acid sites in producing NH_4^+ ions as active NH_3 species, although with different reaction schemes [60-64]. However, there is disagreement on the activation mode of NH_3 over the catalysts, as discussed below.

Regarding the coordination of NH_3 on the catalyst, Eng et al [65] proposed that over zeolite catalysts, pairs of neighboring Brønsted acid sites are necessary for adsorption of NH_3 ; such that the adsorbed NH_3 molecules are close enough together that they can both bond with other reactant molecules. They also proposed that NH_3 must be adsorbed through the three hydrogen bonds in order to be reactive for SCR.

There can be many forms of intermediates when NH_3 is adsorbed on catalyst surfaces. Researchers [56] studied the activation form of NH_3 over Lewis acid sites and found that, after being coordinated on the catalyst surface, NH_3 undergoes hydrogen abstraction and gives rise either to $-\text{NH}_2$ amide species or to its dimeric N_2H_4 form, hydrazine. Other species tentatively identified as imide (NH), itroxyl (HNO), nitrogen anions (N_2^-), and azide anions (N_3^-) are also produced [56]. Their conclusions are supported by Amores et al [66], who also reported that due to the high activity of the intermediates listed above, no adsorbed species other than coordinated NH_3 can be found in significant amounts on the catalyst surface. Lietti et al [67] proposed that over vanadium-based catalysts, NH_3 activation occurred via formation of a V-NH_2 amide species based on their IR experiments.

Tronconi et al [68] found that a simple Langmuir approach would not represent adsorption and desorption data accurately. The best data fit was achieved with a Temkin-type adsorption isotherm where the activation energy for desorption is a function of the surface coverage. They found the activation energy for desorption at zero coverage (E_d°) was close to 25 kcal/mol, while $E_a = 0$ kcal/mol for NH_3 coverage varying from 0 to 80%, within a temperature range of 220 to 500°C, suggesting a non-activated NH_3 adsorption process, which was supported by Amores et al [66].

2.3.2 Standard SCR reaction

The factors that affect catalytic activity have been studied by several groups. One major factor that affects the catalytic activity, as could be concluded by the discussion just presented, is the type and concentration of acid sites. Topsøe et al [62] found that for the standard SCR reaction over a V-based catalyst, the catalytic activity is positively related to the concentration of Brønsted acid sites. Wachs et al [8] suggested that the SCR reaction is faster when the surface acid site is a Brønsted acid site. They also proposed that the standard SCR reaction over a V-based catalyst does not necessarily require two adjacent surface redox sites to proceed, but it appears that the reaction occurs most efficiently over a pair of surface sites containing a surface redox site and an adjacent surface non-reducible metal oxide site [8]. Choi et al [69] observed similar trends with a zeolite-based catalyst, concluding that the surface acidity of mordenite catalysts appears to be a dominant factor in the performance of the SCR reaction system.

Among the components of the gas mixture, O_2 and NH_3 both affect catalytic activity. NH_3 is of course the reducing agent in the system. However, excess gaseous NH_3 appears to inhibit the SCR reaction by limiting access of the NO_x species to adsorption sites within the zeolite [65]. Along this line, reported estimated kinetic order dependencies in NH_3 vary from -0.61 [65], -0.55 to -0.35 [70], to 0 [71]. It also appears that the inhibition decreases with increasing temperature indicating a possible shifting order in NH_3 [7, 35]. In terms of NO , the reaction is consistently agreed to be nearly first order [65, 70-71]. It is also commonly understood that O_2 is necessary for the standard SCR reaction. There has been some discrepancy for the order in O_2 , ranging from 1.06 [65], 0.5 [70] to 0 – 0.13 [71]. Sjøvall et al [7] studied the standard SCR reaction over Cu-ZSM-5 and found that O_2 improves the activity at temperatures below 250°C, but at higher temperatures it decreases the activity. Topsøe et al [62] found that over the V-based catalyst, O_2 is necessary to regenerate Brønsted acid sites and $V=O$, which is supported by Tronconi et al [72]. They also found that at high O_2 partial pressures, the reaction rate is mainly determined by the concentration of Brønsted acid sites and NO partial pressure, whereas at low O_2 partial pressures, surface reoxidation is slow (discussed in the mechanistic aspects below) and the rate becomes dependent on the concentration of $V^{5+}=O$ groups.

Several factors affecting SCR reaction selectivity toward N_2 versus N_2O have been studied. The first factor is catalyst structure. Wachs et al [8] found that the selectivity toward N_2 formation over a V-based catalyst varies with the specific oxide support. For example, they found that among the supports tested, the performance was $TiO_2 > Al_2O_3 > SiO_2$. They also found that the selectivity toward N_2 decreased with the concentration of pairs of redox sites, too much of which will result in N_2O . Kieger et al [73] studied the standard SCR reaction over Cu-FAU and found that CuO aggregates lead to significant formation of N_2O . Delahay et al also studied N_2O formation during NO_x SCR on Cu-FAU and found that besides CuO aggregates, N_2O could also form in the presence of NNN Cu ions, which may be similar to $-HN-(CH_2)_2-$

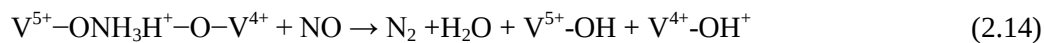
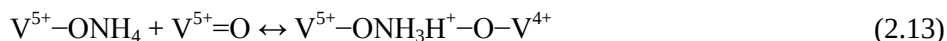
$\text{NH}-(\text{CH}_2)_2-\text{NH}(\text{CH}_2)_3-\text{Cu}^+$, located within the sodalite cages. N_2O formation on NNN Cu ions increases with the amount of NO_2 in the feed, resulting from the interaction of NO_2 with NH_3 , explained in further detail below. The formation of N_2O from 350 to 750K can be lowered very significantly by dedicated preparation of Cu-FAU based catalysts, and in particular by the occupation of sites in sodalite cages with dedicated co-cations, e.g. Ba. [74] The second factor affecting selectivity is temperature. Wachs et al [8] found that the selectivity toward N_2 over a V-based catalyst decreases with temperature due to increased oxidation of NH_3 . Their conclusion has been supported by many groups [7, 73, 75-77]. Kim et al studied SCR reactions over a metal/zeolite catalyst and observed that N_2O was formed from two distinct reactions [78]. At relatively lower temperatures, beginning below 200°C, N_2O is formed via equations (2.9) and (2.10). At temperatures above 400°C, the oxidation of NH_3 by O_2 can produce N_2O by the following reaction (2.11).



The third factor that affects N_2O formation is the ratio of NO_2 to NO as NO_x . The thermal decomposition of ammonium nitrate is a standard method to produce N_2O in the laboratory [52]. A combination of low temperatures and high NO_2/NO_x ratios can cause the formation of ammonium nitrate on the catalyst surface on both Fe- and Cu-zeolite catalysts [79]. Kamasamudram et al found that the evolution of N_2O and N_2 during the subsequent temperature-programmed desorption experiments after SCR reactions were only pronounced at conditions conducive to the formation of ammonium nitrate, such as temperatures below 250°C and over-equimolar ratios of NO_2 and NO [54]. Last, but not the least, water [57], particularly at high temperature, can help maintain high NO conversions and high N_2 selectivity over V-based catalysts because it can hinder the oxidation of NH_3 . Therefore, water improves the catalyst performance and widens the temperature window of the SCR reaction towards higher temperatures.

Eley-Rideal and Langmuir-Hinshelwood mechanisms have been proposed for the standard SCR reaction. Those who proposed the Eley-Rideal mechanism argued that on a V/ TiO_2 catalyst NO does not adsorb on the surface because it is covered by NH_3 , which has greater basicity and blocks the Ti^{4+} adsorption sites. These data are in good agreement with kinetic observations on V-based catalysts where zero/negative and first order kinetics are observed with respect to NH_3 and NO , respectively [35, 80-81]. Those who supported the Langmuir-Hinshelwood mechanism [8, 69] proposed that SCR proceeds most efficiently over a dual-site mechanism involving a surface vanadia redox site and an adjacent surface non-reducible metal oxide site. Eng et al [65] thought that NO can absorb weakly on the catalyst surface to form NO^+ and NO_2 , even though it is unclear how NO_2 adsorbs at reaction temperatures since NO_x TPD results indicate negligible adsorption of NO_2 onto H-ZSM-5 at temperatures above 200°C. It appears that further research is needed to characterize the SCR reaction mechanism.

Based on current literature, a lot of work has focused on the redox cycle on V-based catalysts, while less is known for zeolite-based catalysts. For V-based catalysts, Topsøe et al [62] suggested that the activation of NH₃ involves a transfer, or a partial transfer, of hydrogen and reduced V-OH groups as a product. The O₂ regenerates the V⁵⁺=O surface species. They proposed the following redox reaction sequence:



As a summary of the reaction steps, Tronconi et al [72] proposed a redox scheme for the standard SCR reaction over V-based catalysts, in which vanadium sites are reduced by the reaction between NO and NH₃ and reoxidized by O₂, as shown in Figure 2.1.

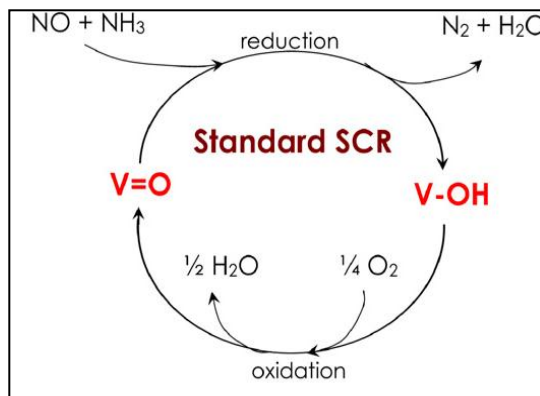


Figure 2.1 Standard SCR redox scheme over V-based catalyst [72]

Over zeolite-based catalysts, Eng et al [65] proposed that the main role of O₂ is to react with NO to form an active intermediate species, such as NO₂ or NO⁺. They also proposed it as the rate limiting step, which is supported by many groups [70-71, 82-83]. Eng et al [65] proposed the reaction steps as follows:

- (1) Adsorption of NH₃ onto neighboring acid sites and rearrangement of the NH₄⁺ complexes to the 3H structure;
- (2) Reaction of adsorbed NH₃ with NO₂ to form an active complex, which reacts rapidly with NO or NO₂ to form N₂ or N₂O, respectively, leaving a residual complex; and
- (3) Decomposition of the residual complex to form additional N₂ and H₂O.

In terms of the metal species (i.e. the Cu or Fe), for the standard SCR reaction over Cu-FAU, Kieger et al [73] suggested that the Cu ions undergo a Cu²⁺ ↔ Cu⁺ redox mechanism, in which Cu²⁺ is reduced to Cu⁺ by NO + NH₃ and Cu⁺ is oxidized to Cu²⁺ by NO + O₂, with evolution of N₂ and H₂O.

2.3.3 Fast SCR reaction

In order to increase their efficiency, SCR systems come with an upstream oxidation catalyst to oxidize some of the NO to NO₂, so that the fast SCR reaction can occur. Nova et al [84] studied the fast SCR reaction over V₂O₅-WO₃/TiO₂ and found that the highest NO_x conversion was achieved with an equimolar NO₂/NO feed ratio as would be expected based on the stoichiometry shown above (Equation 2.2). The benefits from NO₂ addition to the system were more evident below 250°C, where the activity of the standard SCR reaction is limited. They also found that excess NO₂ with respect to the equimolar NO₂/NO ratio resulted in decreased NO_x conversion. For the fast SCR system, the reaction sequence is similar for both V-based and zeolite-based catalysts, and involves a NH₄NO₃ or related surface species as an intermediate,



The redox reaction between NO and nitrates is the rate-controlling step and is also inhibited by NH₃. Tronconi et al [72] summarized the proposed redox scheme for the fast SCR reaction over V-based catalysts, in which vanadium sites are reduced by the reaction between NO and NH₃ and reoxidized by nitrates, with NO₂ disproportionation over other non-reducible oxide catalyst components, as shown in Figure 2.2. The reaction scheme for NO/NO₂-NH₃ SCR over Fe-ZSM-5 at low temperature was proposed by Grossale et al [6] based on their transient study results. The scheme is as shown in Figure 2.3. They proposed that NO oxidation by nitrate was the rate limiting step in the system.

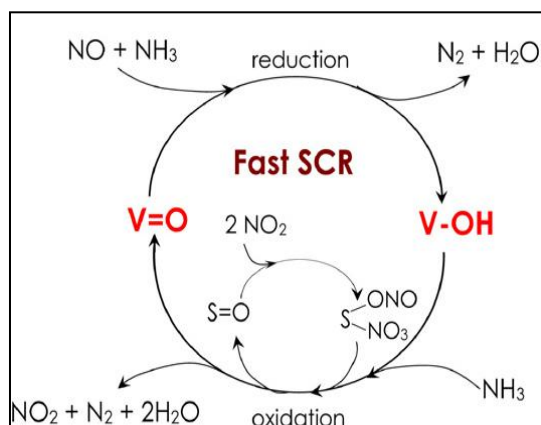


Figure 2.2 Fast SCR redox scheme over V-based catalyst [72]

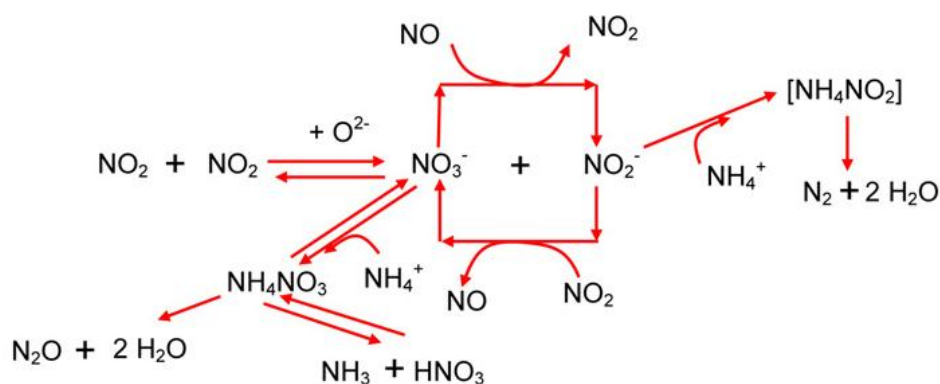


Figure 2.3 Proposed scheme for NO/NO₂-NH₃ SCR over Fe-ZSM-5 at low temperature [6]

Colombo et al [85]Massimo Colombo; Isabella Nova; Enrico Tronconi, Catalysis Today 197(2012) 243-255] recently proposed a detailed kinetic model of NH₃-NO/NO₂ SCR reactions over a Cu-zeolite catalyst. The graphical abstract is shown in Figure 2.4. In this model, thirteen reactions are considered, including NH₃, NO₂ adsorption and desorption, nitrate decomposition, nitrite oxidation, and the reduction of nitrates and nitrites by NH₃.

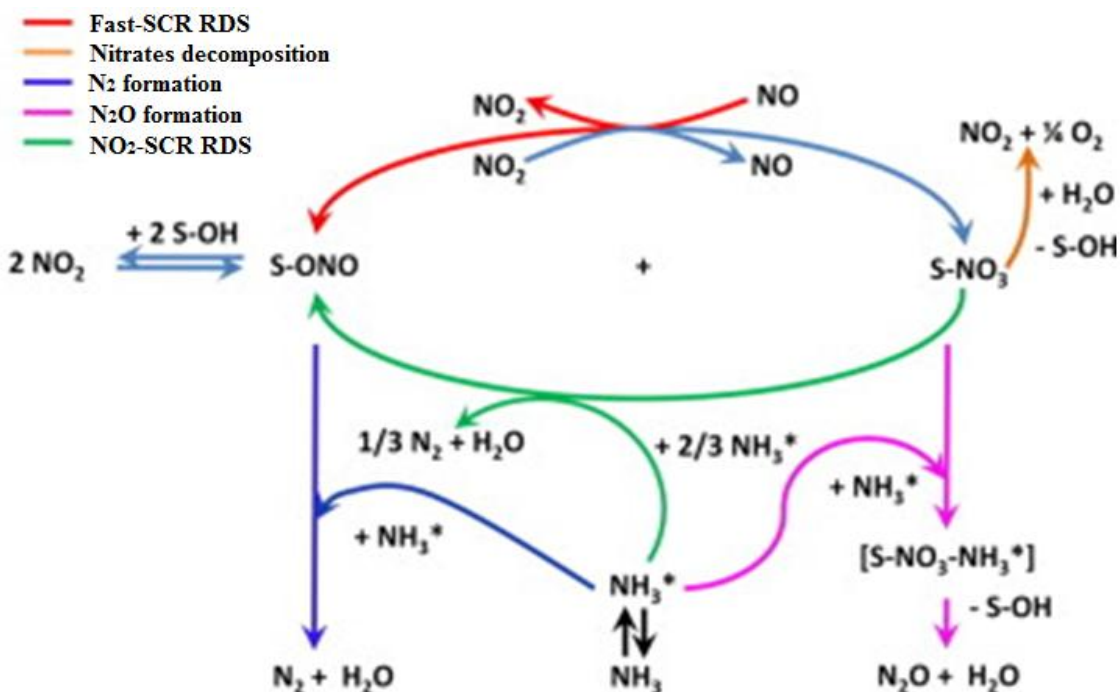


Figure 2.4 Graphical abstract of detailed kinetic model of NH₃-NO/NO₂ SCR reactions over Cu-zeolite catalyst.

2.3.4 The role of NO₂ in SCR reactions

The difference between standard and fast SCR reactions has been addressed in great detail, especially on Fe- and Cu-zeolites. The relative NO₂ amount of NO_x has an important impact on SCR reaction rates. However, the cause of the difference is still under investigation. The core question is what is the role of NO₂ in SCR reactions.

Many groups agree that the effect of NO₂ in the V-based catalytic system is to serve as a more efficient oxidizing agent, in comparison to O₂, for the vanadium sites resulting in an increased reaction rate [52, 86-88]. Koebel et al [87] extensively investigated the reaction of NH₃ with NO/NO₂ on vanadia-based catalysts. The NO₂-enhanced reoxidation of the catalyst was demonstrated by in-situ Raman experiments over V₂O₅/TiO₂ and they found that the V⁺⁴ species formed during the reduction of NO with NH₃ were reoxidized faster by NO₂ than by O₂, resulting in an increased reaction rate of the fast SCR reaction. Tronconi et al [72] investigated the redox mechanism governing the SCR of NO/NO₂ by NH₃ at low temperature using transient reactive experiments over a commercial V₂O₅/WO₃/TiO₂ catalyst. With temperature-programmed reaction runs, they found that NO₂ and HNO₃ were able to reoxidize the V catalyst at much lower temperature than O₂. At temperatures below 250°C, NO₂ can significantly enhance the NO + NH₃ reactivity via the buildup of adsorbed nitrates, which they found could be decomposed above 250°C. They proposed a unifying redox approach for the overall NO/NO₂-NH₃ SCR chemistry over V-based catalysts, in which vanadium sites are reduced by the reaction between NO and NH₃ and are reoxidized either by oxygen (standard SCR) or by nitrates (fast SCR), with the latter formed via NO₂ disproportion over other non-reducible oxide catalyst components. Based on transient reaction experiments, Grossale et al [6] proposed that the fast SCR reaction proceeds at low temperature on Fe-ZSM-5 catalyst via a global sequence involving NH₄NO₃ or related surface species as intermediates,



Such a sequential scheme is the same as that proposed for the fast SCR (Equations 2.17 and 2.18) over V-based catalysts and other zeolite catalysts and thus is considered a general mechanism. They showed that the redox reaction between NO and nitrates is the rate-controlling step and is inhibited by NH₃. A general summary of the fast SCR chemistry over V-based and zeolite catalysts that emphasizes the key role of surface nitrates was given.

The role of NO₂ in SCR over Fe-ZSM-5 catalysts has also been investigated by Schwidder et al [90] who found that standard and fast SCR require different Fe sites. Standard SCR proceeds both on isolated and oligomeric Fe oxo sites, whereas a small concentration of isolated Fe sites is sufficient to sustain the high reaction rates of fast SCR, with no discernible contribution of different sites. In addition, strong deactivation in standard SCR accompanied by increasing NH₃ oxidation activity does not occur in fast

SCR, suggesting that those isolated sites, which are responsible for fast SCR, are very resistive toward clustering under automobile exhaust conditions .

2.3.5 NH₃ oxidation

NH₃ oxidation by O₂ in SCR systems, called parasitic NH₃ oxidation [54], is a competitive reaction with the reactions between NH₃ and NO_x. Kamasamudram et al found that parasitic NH₃ oxidation exhibited complex dependencies on the process parameters, such as temperature and concentration, due to the competition between NH₃ reactions with NO_x and oxygen. They observed that with O₂ as the only oxidant in the system, the NH₃ + O₂ reaction is not pronounced at lower temperatures, but with the presence of NO_x some parasitic NH₃ oxidation is apparent at such temperatures. They suggested that NH₃ might be oxidized by NO_x without reducing the latter to N₂ or N₂O. Girard et al investigated the influence of NH₃ to NO_x ratio on SCR performance and found that at higher temperatures, more NH₃ is needed to improve NO_x conversion [91], to overcome the parasitic oxidation.

2.3.6 NO oxidation

NO oxidation is likely an important step for SCR, as nitrate formation seems a key step in the reaction process. NO oxidation experiments and models have been done by several groups [7, 92-97]. NO oxidation is usually limited by the kinetics at low temperatures and by thermodynamic equilibrium at high temperatures [98]. Metkar et al [93] found that the NO oxidation reaction was equilibrium limited for temperatures higher than 350°C. At low temperature, Olsson et al observed that NO oxidation could occur even at room temperature over a Cu-ZSM-5 catalyst. They suggested that this low-temperature NO oxidation occurs with species loosely bound on the surface [92]. NO oxidation showed close resemblance with the standard SCR reaction when comparing the reaction rates, activation energies and the reaction orders with respect to NO and O₂, which supports the proposed idea in some literature that the NO oxidation is the rate determining step in standard SCR reaction. The presence of water showed strong inhibition on NO oxidation reaction over an Fe-ZSM-5 catalyst [93].

2.4 SCR catalyst deactivation studies

It is not enough for a catalyst to be highly active; the catalyst must also be durable. For practical purposes, three main classes of catalyst deactivation can be distinguished: chemical, thermal, and mechanical. On the other hand, deactivation can be categorized as reversible (temporary) and irreversible (permanent). In diesel engine systems, factors such as the presence of hydrocarbons, SO₂, gas-stream impurities and soot, high exhaust gas temperatures, and vibration can cause the three kinds of deactivation for SCR catalysts. For zeolite-based SCR catalysts, the primary poisoning chemicals are SO₂, H₂O, P, and hydrocarbons. Temperature, especially high temperature, is another important factor that deactivates zeolite-based SCR catalysts. The extent of the thermal degradation also depends heavily on the presence of water.

In terms of SO_2 , Kim et al [99] found that for mordenite-type zeolite catalysts, the catalyst was deactivated via formation of surface sulfate species. The authors concluded that the sulfate species did not alter the chemical environment of the copper ions contained in the zeolite catalysts. Deactivation was primarily caused by blocking the active sites responsible for the reaction between the adsorbed NH_3 and NO. For Fe-zeolite catalysts, Silver et al [100] found that when sulfur is less than 350 ppm in the inlet stream, it did not affect the activity. Other authors [38-39, 101] however, found that for Fe-ZSM-5 catalysts, when the reaction temperature is below 300°C , SO_2 decreased SCR activity, whereas it actually improved activity at high temperatures. At low temperature in the presence of water, large amounts of ammonium sulfate salts formed on the catalyst surface resulting in catalyst pores being blocked and catalyst deactivation, while at high temperature, just a small amount of ammonium sulfate salts formed on the catalyst surface, which promotes SCR activity due to the reaction between NO and ammonium-sulfate salt [102]. The different impacts of SO_2 and SO_3 on Cu-zeolite SCR catalysts were investigated by Cheng et al [103], who found that SO_3 poisoning caused more significant deactivation of Cu-zeolite catalysts than SO_2 with the presence of H_2O .

The effect of P on Fe-zeolite catalyst performance was also studied by Silver et al [100], who found that P causes decreased NO_x conversion and an increase in NH_3 slip. They believed that P blocked adsorption sites and channels, primarily at the inlet of the monolith, causing a loss of NH_3 storage capacity. Activity was then reduced due to the decreased amount of adsorbed NH_3 .

The effect of water on the SCR reaction is complicated and still debated, especially at low temperatures. Nova et al [35] found that the presence of water at low temperature is detrimental to the SCR reaction over a V-based catalyst. Over Cu-ZSM-5 catalysts, Sjoval et al [7] and Sullivan et al [104] found that water can enhance the SCR reaction over a wide temperature range, from 100°C to 500°C . The complexity of the effect of water on SCR is because water can affect several of the reaction steps in the overall SCR reaction. For example, water has a negative effect on NO and NH_3 oxidation [7, 105], of which the former is detrimental and the latter is beneficial to SCR reactivity. In addition, water affects NH_3 adsorption and desorption onto or from the catalyst according to Sjoval et al [106] and Nova et al [35]. Although water exerts a detrimental effect on certain reactions, no detectable irreversible catalyst deactivation was observed for all the catalysts [38].

High temperature exposure can cause deactivation, for which two kinds of mechanisms have been proposed, dealumination and sintering. In terms of steam-induced dealumination, the lattice aluminum can migrate towards extra framework positions and result in structural degradation in the reaction process. Pieterse et al [108] found that the deactivation of zeolite-based cobalt and palladium catalysts is caused by temperature-induced ion migration and sintering. They suggested that the activity and selectivity could be maintained if the catalyst operated at temperatures not exceeding $350\text{--}400^\circ\text{C}$, where deactivation is not

significant. Grinsted et al [109] proposed that dealumination leads to loss of Brønsted acid sites and destruction of the zeolite for Cu-ZSM-5. It was observed that the activity decreased rapidly at 410°C if the catalyst is exposed to steam-containing air, whereas it is not affected by dry air. The activity decreased to about half its initial value and remained constant thereafter. The work done by Petunchi and Hall [110] supported the conclusion of Grinsted et al qualitatively.

The copper content of the catalyst impacts the resistance to dealumination [109, 111-112] for various zeolite structures, including MFI, MOR, FER, BEA, and FAU. The introduction of the Cu^{2+} before steaming preserves these sites from total destruction and only more local transformations take place. According to Kuchеров et al [112], when both Cu^{2+} and Al^{3+} ions are present in the ZSM-5 framework, the structure of the framework would be more flexible to stand the stress exerted on it.

Karas et al [113] proposed that the thermal deactivation of Cu-ZSM-5 is mainly caused by the sintering of copper. They found that brief periods of catalytic use at temperatures of 600–800°C result in substantial deactivation and substantial losses of micropore volume. As the temperature was increased, a substantial amount of copper was sintered to CuO, or perhaps Cu_2O , accompanied by loss in zeolite crystallinity. They proposed that CuO crystallites grow primarily in the interior surfaces of this zeolite. As these crystallites exceed critical sizes, local zeolite structure is destroyed, which causes a loss of micropore volume. Their conclusions were supported by the work done by Park et al [111] who studied sintering of Cu-ZSM-5 catalysts as well. For Fe-ZSM-5, similar results were found by Krishna et al [114] who found that when Fe-ZSM-5 catalysts were aged at 600°C for prolonged times, Fe^{3+} from the ion-exchange positions were changed into FeOx. The detachment of Fe^{3+} led to further extensive zeolite dealumination. It is worth noting that zeolites with the Chabazite (CHA) structure and containing small radius ($\sim 3.8 \text{ \AA}$) ring pores have been gaining more attention due to their superior resistance to thermal aging [44-45]. Kwak et al [115] investigated the effects of high-temperature hydrothermal treatment on Cu species, zeolite framework structure and on NO reduction activity using model Cu-zeolite catalysts, including Cu-SSZ-13, Cu-beta, Cu-ZSM-5 and Cu-Y, where only Cu-SSZ-13 has the CHA structure. They found that after hydrothermal treatment at 800°C for 16 h, Cu-SSZ-13 showed essentially no change in NOx reduction activity, while Cu-Y completely lost its NH_3 SCR activity. Both Cu-ZSM-5 and Cu-BEA were found to lose NOx reduction activity primarily at low temperatures ($< 350^\circ\text{C}$). Under fast SCR conditions, significant amounts of N_2O were produced over the aged Cu-ZSM-5 and Cu-BEA at all temperatures. With XRD, they found that the zeolite structure remained largely intact for all the Cu-zeolite catalysts following hydrothermal aging, except for Cu-Y. For the aged Cu-ZSM-5 and Cu-beta catalysts, some dealumination was observed, while little change was seen for Cu-SSZ-13. When the redox behavior of Cu species was examined using H_2 -TPR, they found that Cu^{2+} could be reduced to Cu^+ and to Cu^0 in Cu-ZSM-5 and Cu-beta, while Cu^{2+} could be reduced to Cu^+ only in Cu-SSZ-13. After hydrothermal aging,

CuO and Cu-aluminate like species were found to form in Cu-ZSM-5 and Cu-beta, while again little change was observed for Cu-SSZ-13, consistent with the minor changes in the SCR activity of this latter catalyst. Thermal durability of Cu-CHA NH₃-SCR catalysts for diesel NO_x reduction has been investigated by Schmieg et al [55]. They found that the zeolite structure collapses in a shorter period of time as the aging temperature increases to more than 800°C. SCR performance deteriorates due to the destruction of zeolite structure and/or Cu agglomeration, which may also be the cause of the reduction in NO/NH₃ oxidation activity and NH₃ storage capacity.

Hydrocarbon (HC) poisoning is another factor that needs to be considered for SCR systems, especially during cold start or when the upstream DOC catalyst is deactivated, through which HCs may slip and interact with NH₃ SCR catalysts. Although they can serve as a reductant in a HC-SCR process, hydrocarbons are typically considered as poisons for NH₃-SCR catalysts [116-117]. In the literature, several mechanisms have been proposed for HC poisoning, including competitive adsorption between the HCs and NH₃, coke formation which blocks pores and/or active sites, inhibition of the formation of required intermediates such as NO₂, and thermal aging caused by residual hydrocarbon oxidation [118-126]. The poisoning effect of hydrocarbons at low temperatures is reversible. Heo et al proposed that over Cu/ZSM-5 and Fe/ZSM-5 catalysts, the primary cause for C₃H₆ inhibition on NH₃-SCR was the competitive adsorption of NH₃ and C₃H₆ on the catalyst surface [118]. Silver et al [100] found that an initial loss of activity due to hydrocarbon exposure at low temperature was reversible simply by ramping the sample up in temperature. At high temperatures, however, the effects of hydrocarbons on SCR reactions are complicated. It may cause coking or form poisonous intermediates. Sultana et al [127] compared the effect of decane on the performance of Cu/NaZSM-5 and Cu/HZSM-5 at 280°C and found that the presence of decane decreased the activity of both catalysts due to coke formation. Cu/HZSM-5 catalyst showed a larger decline in NO_x conversion with time on stream compared to Cu/NaZSM-5. The higher activity of Cu/NaZSM-5 was attributed to the promoting effect of Na⁺ cations in the formation of active Cu⁺ and nitrite and nitrate intermediate species and retardation of coke formation. Besides temperature, the chain length and structure of HC were found to be factors in poisoning as well [121-122]. For example, Devarakonda et al found that toluene has a significant negative effect at low temperature on the SCR reaction, but the impact was less at higher temperatures. Luo et al [117] studied the effects of C₃H₆ on key SCR reactions over a model Cu/beta zeolite catalyst. They found that under standard SCR conditions, C₃H₆ clearly inhibited the reduction reaction at 200°C and above. The inhibition was caused by surface intermediate species formed during C₃H₆ oxidation, including acrolein-like and coke species. Under fast SCR conditions, C₃H₆ also had a negative effect on the target reactions. They found that NO₂ was quickly reduced to NO by C₃H₆, leading to the occurrence of some standard SCR instead of purely fast SCR. However, C₃H₆ had a positive effect on NO₂ SCR. The reduction of NO₂ to

NO by C₃H₆ resulted in the occurrence of the fast SCR reaction combined with NO₂ SCR instead of pure NO₂ SCR. The reaction pathway change also decreased N₂O formation significantly.

2.5 Kinetic modeling of the SCR DeNO_x system

In order to minimize emissions during operation, and account for different driving scenarios, a predictive control strategy for the SCR system is desired. Mathematical modeling and simulation are useful in identifying the optimal designs and reducing the amount of experimentation needed to achieve this goal. Mathematical models vary in degree of complexity. Our review will focus on kinetic models which can help us understand the reaction mechanisms, evaluate reaction parameters, as well as predict the reaction outcome of ideal reactors.

A primary purpose of kinetic modeling is to determine the parameters in the reaction rate expression, namely the concentration dependencies, and activation energy. Because the SCR reaction system is complicated, it is reasonable to separate the system into several basic steps, such as NH₃ adsorption, NO and NH₃ oxidation, and the actual SCR step. There are two ways to describe reaction rates: one is via a global model, and the other is called the intrinsic model, which describes the process based on the reaction mechanism and includes the mechanistic steps.

The advantage of the global rate expression is that it is convenient to apply. The drawback of this method is that its application may be limited because the SCR process is too complicated to be expressed with one simple rate expression. The reaction mechanism itself may depend on temperature, concentration and the composition of the reaction system, which may keep changing in real situations.

A typical global model for the SCR reaction was developed by Yim et al [128] and Baik et al [129] who studied the standard SCR reaction with urea over a Cu-ZSM-5 catalyst. The authors first assumed that there were four reactions in the system, including thermal decomposition of urea, catalytic decomposition of urea, hydrolysis of HNCO and the SCR reaction over the catalyst. Secondly, they obtained the standard reaction parameters by assuming the surface reaction as the rate limiting step. As an example, one of their key expressions of reaction rates is as follows.

$$\begin{aligned}
 -d\text{CNH}_3/dt = & k_1\text{CNOCNH}_3 / (1 + \text{KNOCNO})(1 + \text{KNH}_3\text{CNH}_3) \\
 & + k_2\text{CNH}_3 / (1 + \text{KNH}_3\text{CNH}_3) \\
 & - k_3\text{C}_{\text{Urea}} - k_4\text{C}_{\text{NHCO}}\text{CH}_2\text{O}
 \end{aligned} \tag{2.21}$$

Many researchers have studied the intrinsic SCR reaction steps. The drawback of this method is that the process is tedious, as there are many steps that need to be studied and many parameters to evaluate. But again, the advantage of this method is that the description of the process is more chemically accurate and the evaluated parameters typically span a larger range of operating parameters. For the last several years, in the field of SCR with NH₃ over zeolite-based catalysts, notable work has been done by groups led by Olsson [130] and Tronconi et al [6].

According to Olsson et al [130], the SCR reaction model could be separated into seven parts as follows:

- (1) NH_3 adsorption and desorption;
- (2) NH_3 oxidation;
- (3) NO oxidation;
- (4) standard SCR ($\text{NO} + \text{O}_2 + \text{NH}_3$);
- (5) fast SCR ($\text{NO} + \text{NO}_2 + \text{NH}_3$);
- (6) NO_2 SCR ($\text{NO}_2 + \text{NH}_3$); and
- (7) N_2O formation

In their model [131], the reaction processes were broken down into 22 reactions. There were four kinds of active sites in their model, described as S1a (Cu site), S1b (Cu site), S2 (Brønsted acid site) and S3 (site for weakly bound species). Over those sites, different species could be adsorbed.

The model parameters were evaluated and validated with transient reactions. The effect of mass transfer from the gas to the surface was described with a diffuse interface model and the mass transfer coefficient was calculated using the Sherwood number.

In order to obtain reaction parameters for those reaction steps, various experiments were conducted. One of the key experimental results built into their model was that there are four NH_3 molecules adsorbed per copper [132-133].

From their experiments, they found that the adsorption of NO_2 was significantly less than NH_3 and they assumed that NO_2 can only adsorb on S1a sites. They found that at temperatures as low as 30°C , significant adsorption of NH_3 occurred, so they added S3 sites in the model to describe this phenomenon. Water was found to reduce NH_3 storage, so the inhibition of water was taken into account in the model. The catalyst adsorbed large amounts of NO_2 relative to NO. Therefore, NO adsorption was not included in the model. NO_2 [92] TPD experiments were used together with NO oxidation experiments in developing a detailed kinetic model for NO oxidation.

It is worthwhile to mention that Grossale et al [6] studied the fast SCR reaction model over Fe-ZSM-5. They proposed seven elementary reaction steps and built a relationship between the observed global reaction description and the elementary steps. Some of their key findings are as follows.

1. The reduction of nitrates by NO as in reaction (2.20) is rate-controlling at low temperature.
2. NH_3 inhibits the reaction likely by blocking the surface nitrates, i.e. high NH_3 concentrations have a detrimental effect on fast SCR kinetics at low temperature.
3. When the catalyst is saturated with nitrates, the fast SCR reaction can go on in the absence of gaseous NO_2 .

These former studies provide a good basis for describing the SCR reaction in ideal situations. However, there are other steps that need to be incorporated into the modeling system. For example, it is known that

hydrocarbons can have an effect on the outcome of the SCR reaction, therefore, it necessary for us to consider this factor. Other factors, such as thermal deactivation and chemical deactivation, cannot be ignored, and have not been considered to date based on our knowledge.

2.6 Design of SCR reaction system

A general layout of a urea-SCR system for diesel engine applications is shown in Figure 2.5. As shown, there are two catalysts, a pre-oxidation catalyst and the SCR catalyst.

The combined requirements of compactness, high volumetric flow rates and low back pressure resulted in monolith supported systems for automotive catalysts since the 1970's [3, 134-135]. The monolith is made of a ceramic material and consists of a large number of thin walled, narrow, parallel flow channels with square, triangular or honeycomb configurations. The catalyst is deposited on the walls of the narrow channels as a thin layer of porous washcoat. The gas that enters the reactor is transported by convection and diffusion in parallel flow streams through these narrow channels and reactions occur on the active catalytic surfaces present in the washcoat.

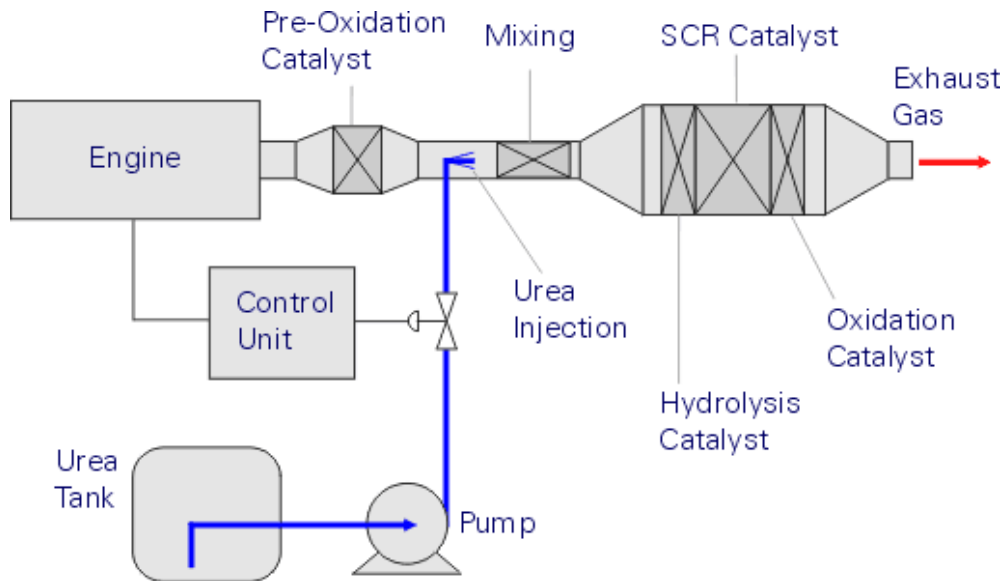


Figure 2.5 Urea SCR system for mobile diesel engine [9]

The primary functions of the pre-oxidation catalyst are to oxidize NO, hydrocarbons and CO in the exhaust gas. Increasing the SCR catalyst activity at low temperatures is a big challenge, with one solution being to facilitate the fast SCR reaction. Thus a 1:1 NO:NO₂ ratio is targeted, with a 9:1 NO:NO₂ ratio typical of engine exhaust [52]. Thus NO₂ production is critical, since operating temperatures frequently are low in diesel exhaust.

Urea is typically used as the NH₃ precursor. The urea solution is pumped from the urea tank and sprayed through an atomizing nozzle into the exhaust gas stream. The urea is injected into the exhaust stream at a

controlled rate, which is a function of engine speed and load. Thorough mixing of urea with exhaust gases and uniform flow distribution are very important in achieving high NO_x conversions. Upon mixing with the hot exhaust gas, urea undergoes hydrolysis and thermal decomposition producing NH₃. In some systems, urea hydrolysis is additionally promoted by a hydrolysis catalyst installed upstream of the SCR catalyst [9]. Another design includes the urea hydrolysis formulation zone-coated [9] on the inlet portion of the SCR catalyst.

Under certain conditions, some unconsumed NH₃ will slip from the SCR catalyst. For example, sometimes more than enough urea will be injected into the system to increase deNO_x efficiency and [136] excess NH₃ will be released into the environment. In order to minimize the amount of released NH₃, another catalytic device downstream from the SCR converter is added. One of the designs recently proposed in the literature [137] relies on the implementation of bi-functional dual-layer catalysts, where the lower layer contains a PGM (Platinum Group Metal) based catalyst to oxidize NH₃, while the upper layer consists of an SCR catalyst to reduce the formed NO_x with entering NH₃.

Early studies showed that when NO_x is reduced over TWCs and LNT catalysts, NH₃ could form as a byproduct [28, 138]. Based on such findings, the concept of passive NH₃ SCR was recently proposed [139]. In this system, NH₃ is produced during rich operation, via reduction of the NO_x over the TWC, or LNT. The produced NH₃ is then stored on the downstream SCR catalyst, and can be used as the reductant to reduce NO_x during subsequent lean operation. So, for passive SCR systems, instead of supplying NH₃ via for example urea addition into the exhaust stream, NH₃ is produced on an upstream catalyst, and is then adsorbed on the SCR catalyst and used to reduce NO_x to N₂. Chatterjee et al developed global kinetic models for the LNT + SCR catalysts, considering the accumulation of NO_x and O₂ in the LNT and the adsorbed NH₃ in the SCR. The performance of this hybrid system was simulated with varying temperature and rich phase length, and their effects on NO_x conversions and NH₃ yields were evaluated. The combined system provides better deNO_x efficiency than a single LNT in a wide range of operating conditions, particularly at lower to intermediate temperatures. At high operating temperatures the performance of the added SCR may become limited by a loss of the NH₃ adsorption capacity, and in that case it is advantageous to locate the SCR reactor at a cooler place downstream in the exhaust gas line [140]. Li et al [29], Kim et al [139] and Guralp et al [141] studied passive NH₃ SCR systems for lean-burn spark-ignited, direct injection engines, whose key components include a close-coupled TWC and underfloor SCR catalyst. NH₃ is formed on the TWC with short pulses of rich engine operation and the NH₃ is then stored on the underfloor SCR catalyst. They found that NH₃ formation was highly sensitive to oxygen storage content in the TWC. The capability of SCR catalyst storage for NH₃ and the resistance of SCR catalyst to hydrothermal aging were also very important. In addition, they found that sulfur could

greatly inhibit NH_3 formation on the TWC and hydrocarbon poisoning was challenging due to the low exhaust temperatures.

2.7 Spatial resolution

Spatially resolving reactions is becoming more common as a catalyst testing method in automotive applications, as such methods provide more information than integral (inlet and outlet), steady-state measurements and are therefore quite useful in developing and validating models [142-143]. Figure 2.6 is a schematic of the sampling system used by Horn et al [144] to study the spatial profiles in millisecond partial oxidation processes. Spatially Resolved Capillary Inlet Mass Spectrometry (SpaciMS) has been used to measure gas-phase concentrations along LNT catalysts, and to investigate activity changes with exposure to sulfur for example [145-146]. These studies have shown different activity regions inside the catalyst and how they change as a function of sulfur poisoning. SpaciMS has also been used to monitor competitive reactions along a Diesel Oxidation Catalyst (DOC) and apparent NO oxidation inhibition in the presence of hydrocarbons [143, 147-148]. Spatially-resolved gas-phase concentrations as well as temperatures at the catalyst surface have been measured during C_3H_6 oxidation before and after homogeneous and heterogeneous thermal degradation [142, 149]. From the investigation of the spatial distribution of NOx storage and intermediate gas species in determining the performance of a lean NOx trap catalyst under lean/rich cycling conditions, it was found that stored NOx was significantly redistributed along the monolith axis during the rich phase of the cycle by release and subsequent downstream re-adsorption [150]. Such spatially resolved reaction 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 catalyst length, volume and distribution of active species. 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 [142-143, 146-148, 151]. It is worth pointing out that instead of using a capillary to sample gases at different points in a reactor; other methods were developed to resolve reactions spatially. For example, Henry et al [152] axially resolved the performance of Cu-Zeolite SCR catalysts by simply changing the length of the catalyst.

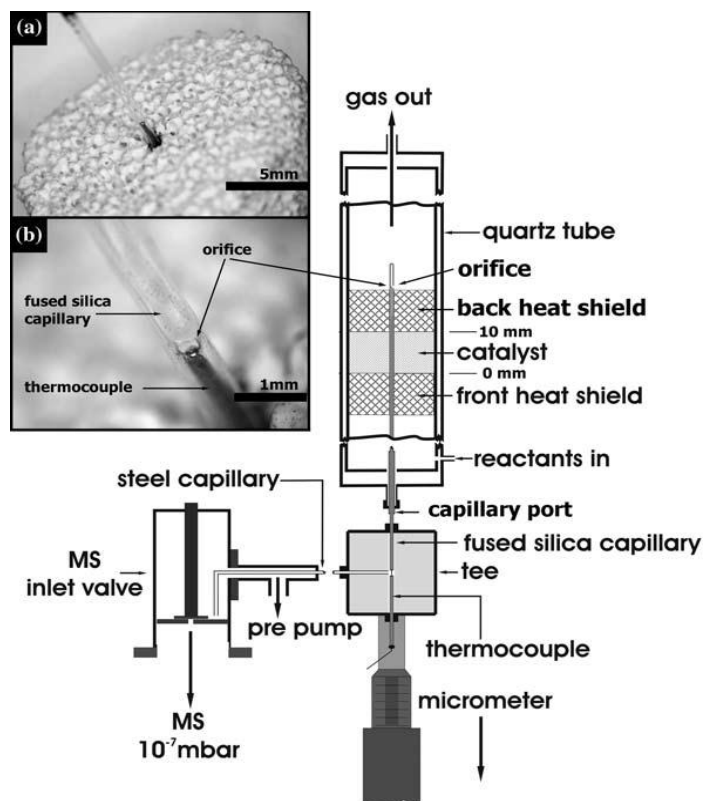


Figure 2.6 Schematic of the axial sampling system [144]

Chapter 3 Experiment Apparatus

3.1 Process flow schematic

The process flow diagram of the primary reactor system components is shown in Figure 3.1. The experiments in Chapter 4 were performed at the University of Waterloo and those in Chapter 5 and 6 were performed at General Motors Global R&D. The two sets of experimental apparatus are similar, except for the water addition units and the nitrogen supply. The water addition unit at the University of Waterloo was a controlled evaporator and mixer unit supplied by Bronkhorst®, while at GM the water was pumped into the system with a pump supplied by Chrom Tech ® and vaporized with an electric heater.

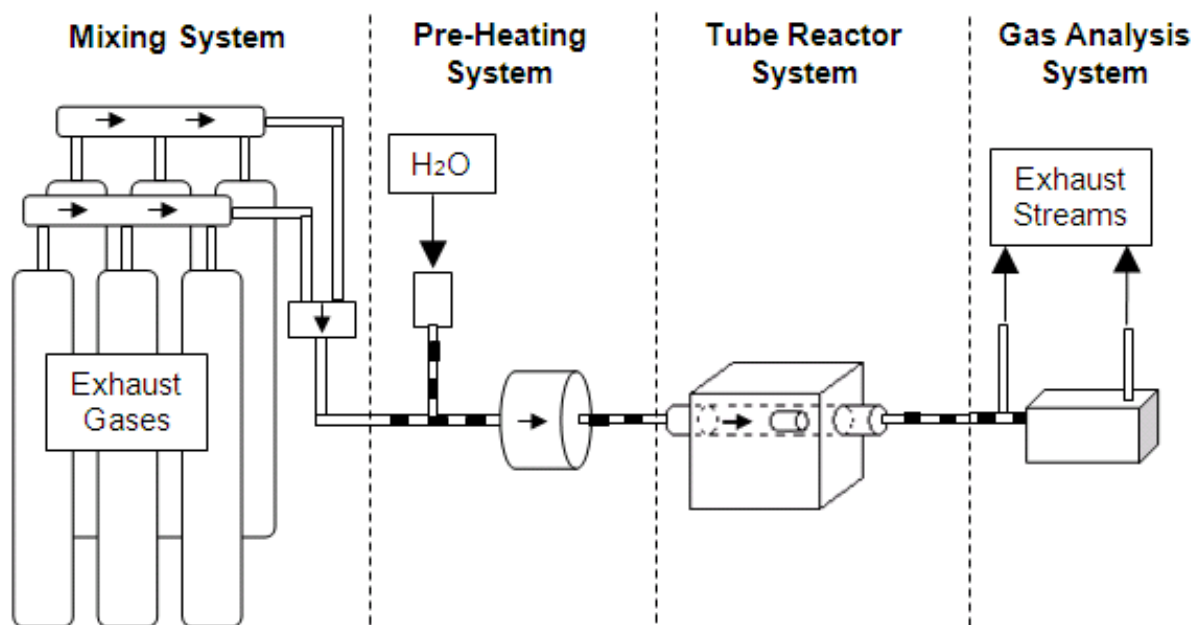


Figure 3.1 Tubular reactor flow diagram

The capillary sampling unit that was used to spatially resolve the reactions is described by Figure 3.2. The gases are sampled through a capillary, which can be moved back and forth within a channel in the monolith. The sampled gases can be mixed with diluting nitrogen, which carries the sample to the FTIR quickly, shortening the response time of the analyzer, and it was also found that the FTIR needed a minimum flow rate for accurate calibrations.

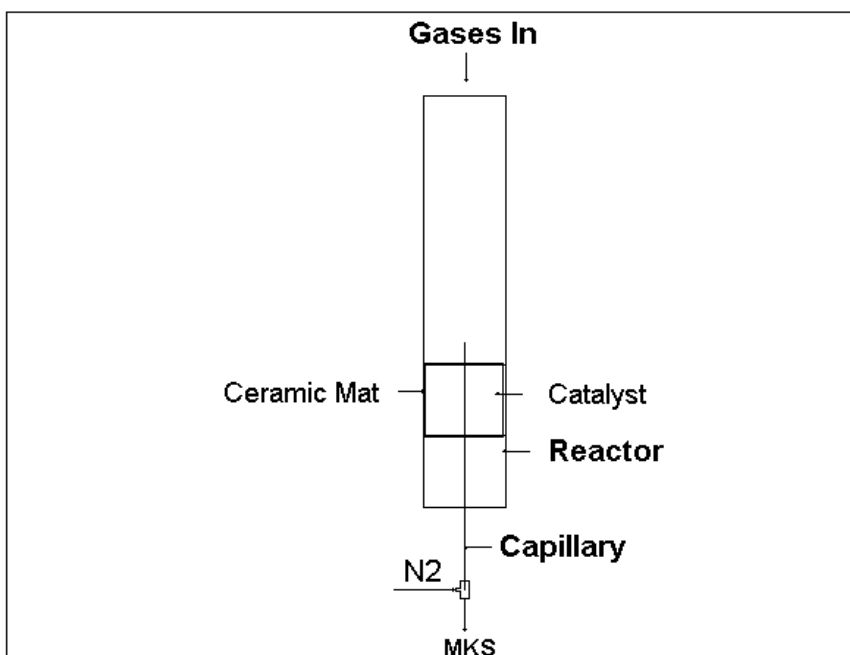


Figure 3.2 Capillary sampling unit

3.2 Gas mixing system

Automobile exhaust gas was simulated by mixing gases from gas cylinders supplied by Praxair. The volumetric flow rates of the incoming gases were controlled by Bronkhorst® mass flow controllers. Carrier nitrogen was provided using a nitrogen generator, manufactured by On Site Gas Systems or via gas cylinders. Moisture was prepared and metered with a Bronkhorst Controlled Evaporator Mixer or a Chrom Tech ® pump.

3.3 Preheating

Preheating the gas mixture is necessary before it is introduced into the reactor. First of all, it will prevent the moisture in the mixture from condensing on the upstream tubing surfaces. Secondly, preheating will reduce heat stress on the quartz reactor. Last, but not least, it can help to reduce the temperature gradients along the reactor, making an isothermal reactor/reaction zone possible. The preheating temperature was set at 180°C.

With the entering gas mixture heated, there is the potential for NH_3 reactions along the upstream stainless steel (SS) tubing. To avoid this, NH_3 was introduced into the system separately, right into the quartz tube directly.

3.4 Reactor

The reactor is a quartz tube. The diameter and length of the reactor are 1 and 26 inches, respectively. A Lindberg tube furnace was used to control the temperature of the reactor. The temperatures before, and at the front and back of the catalyst were monitored and recorded using thermocouples.

Small quartz tubes, 4 mm OD and 3 mm ID, 25.4 cm long, were stuffed in the front part of the reactor. The quartz tubes help to preheat the gases. Their high heat capacity and increased heat exchange surface area enable better gas heating, hinder flow development along the reactor length and therefore minimize any temperature and flow profile gradients in the reactor.

The catalyst sample was usually placed toward the outlet part of the quartz tube reactor, allowing the maximum length of reactor to be used to heat the gases and stabilize the temperature, resulting in the minimal temperature difference between the front and back part of the catalyst.

The outlet gases were plumbed to the analyzer using heated tubing. The analyzer outlet gas was exhausted to building exhaust ventilation.

3.5 Gas analysis

The analysis instrument used in this research is an MKS MultiGas 2030 Fourier-transform infrared (FTIR) analyzer. The adsorption spectrum was measured and the concentration of each gas could be calculated using pre-loaded calibrations. CO, CO₂, NO, NO₂, N₂O, C₃H₆, NH₃, and H₂O gas concentrations were measured.

When spatial resolution experiments were conducted, a capillary was used to sample the gas from specific points along the catalyst (Figure 3.2). The sampled gas was diluted with pure nitrogen. The purpose of the diluting nitrogen is to increase the flow rate through the MKS to reduce the residence time in the system and increase the efficiency of testing. Preliminary results also showed that flow rates below ~200 sccm resulted in obviously incorrect concentrations and large variation in the measurements as a function of time. The volumetric flow rate of diluting nitrogen was controlled with a flow meter and the concentration of CO₂ was used as a tracer to monitor and ensure the flow rate of sampled gases from the reactor.

3.6 Catalysts

The catalysts used in the project were supplied by Cummins and GM. The catalysts were placed in the quartz reactor and wrapped with ceramic insulation matting. The matting ensures that no gas can slip around the catalyst. A picture of the tube furnace and the catalyst is shown in Figure 3.3. The gases exiting the reactor were maintained at >80°C to avoid condensation of water, and minimize the reaction in the tubing when gases flow through it.



Figure 3.3 Furnace and reactor

3.7 Types of experiments

In this research, “normal” and spatial resolution tests were conducted, with normal alluding to outlet measurements only. Key SCR reactions were investigated, including NH_3 adsorption and desorption, NH_3 and NO oxidation, standard SCR, fast SCR and NO_2 SCR. Several of these reactions were spatially resolved. The effect of catalyst hydrothermal aging on SCR reactions was also evaluated.

Chapters 4, 5 and 6 are published results and contain further description of the experiments performed as part of the research.

The bulk of this chapter was published in Applied Catalysis B: Environmental. 102 (2011) 110-119. Chapter numbers have been inserted to help the reader, and Figure numbers changed to reflect the chapter number. There is also some redundancy in the introduction and experimental methods description section relative to the chapters already presented as part of the thesis.

Chapter 4 Spatially Resolving Different SCR Reactions over a Fe-zeolite Catalyst

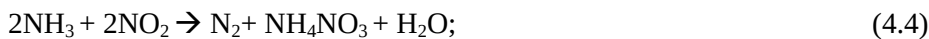
4.1 Introduction

Increasingly stringent emissions regulations have been implemented and proposed in Europe and North America, with examples being Euro VI (2014-15) and Tier II Bin 5 targets [153-154]. Two types of after-treatment technologies, lean NO_x traps (LNTs) and selective catalytic reduction (SCR), have been developed to help meet these regulations. LNTs are primarily being considered for smaller engines (<2.0~2.5 L) because of the cost of the catalyst, which contains noble metals like Pt, Pd and Rh. SCR, which requires urea injection, is emerging as the likely NO_x control strategy for both light-duty and heavy-duty applications. NH₃ is generally used as the reducing agent in SCR because it can be generated on-board via urea hydrolysis (urea-SCR) or on upstream TWCs (three way catalysts) and LNTs (passive SCR) [7,29,155].

Two groups of SCR catalysts, namely vanadia- and zeolite-based, have been commercialized to date [54]. The zeolite-based formulations are considered more thermally stable relative to the vanadia-containing catalysts. This is important due to the volatility and toxicity of the vanadia component-based catalysts, especially if exposed to the heat associated with particulate filter regeneration events. For the zeolite-based catalysts, Cu- and Fe-exchanged formulations are typically studied. Cu-zeolites show very good low temperature performance (below 350°C) while Fe-zeolites exhibit very good high temperature performance. A detailed comparison between Cu- and Fe-based SCR catalysts, in terms of their activity, selectivity, hydrothermal aging, sulfur and hydrocarbon poisoning, can be found in previous work [156-157]. Another advantage of zeolite-based catalysts is their large NH₃ storage capacity, which makes them promising for passive SCR.

Three types of NH₃-SCR reactions have been proposed (as introduced in Chapter 2); the standard, fast and NO₂-SCR reactions [88, 94, 159]. These descriptions are typically associated with the feed NO:NO₂ ratio. Standard SCR (4.1) refers to reaction between NH₃ and NO, with the participation of O₂; fast SCR (4.2) refers to the reaction between NH₃ and an equimolar ratio of NO and NO₂; and NO₂-SCR to N₂ (4.3) refers to reaction between NH₃ and NO₂ in the ratio of 4:3, with the formation of N₂ only. There are some other NO₂-SCR reactions, with a 1:1 consumption of NH₃ and NO₂, including the formation of NH₃ nitrate at low temperatures (4.4) and NO₂-SCR to N₂O (4.5). Generally, the fast reaction has the highest rate and is relatively more active at lower temperature as well. The relative reactivity between the standard SCR and NO₂-SCR reactions varies, depending on the catalyst type. For example, it has been

reported that standard SCR occurs faster than NO₂ SCR on Cu-zeolites catalyst, while slower on Fe-zeolites [160]. Besides these three reactions, other reactions also occur, including NO oxidation to NO₂, and NH₃ oxidation by O₂ (6) which affects selectivity.



Although the three SCR reactions are well studied, a clearer understanding of their relative rates under different NO:NO₂ conditions is required. In application, to take advantage of the fast reaction at low temperatures, an upstream DOC is generally installed to promote the oxidation of NO to NO₂ [161]. NO₂ concentrations will of course fluctuate extensively depending on driving conditions and DOC performance. So, what are the relative rates of the three reactions if the NO:NO₂ ratio is not 1:1? Do the fast, standard and NO₂ SCR reactions occur in parallel or in series? Evaluating the relative reaction extents under different conditions also determines the extent of catalyst use and will help optimize the catalyst length and volume.

Spatially resolving gas concentrations has been applied in several catalytic systems, especially monolith-supported catalysts (SpaciMS). Typically, a fused silica capillary connected to a mass spectrometer is used for gas sampling. By moving the capillary tip to different positions of the catalyst, the concentration of different species can be monitored in-situ, showing where and how quickly different species are formed and consumed along the catalyst length [142, 147-149, 151, 162-164]. SpaciMS has also been used to probe the deactivated area along a catalyst, due to either poisoning or thermal aging [146, 149]. Partridge and coworkers, who developed the technique, have used SpaciMS to evaluate LNT performance and sulfur impact on LNT performance [147, 163-164]. SpaciMS has also been used to study competitive oxidation reactions on a DOC as well as DOC thermal aging [142, 149, 151]. This technique has also been successfully applied in studying the partial oxidation of methane by Schmidt and coworkers [148, 162]. There are no literature-reported SpaciMS data obtained from NH₃-SCR catalysts at the time of this publication. One of the challenges with SCR systems and mass spectrometry is the detection of ppm levels of NH₃ in the presence of relatively high concentrations of H₂O (several percent).

In this study, spatial resolution of gas species during SCR over a Fe-zeolite catalyst was achieved via modification of the SpaciMS technique, specifically by replacing the mass spectrometer with FTIR for gas analysis. The results clearly demonstrate where the different SCR reactions occur along the catalyst as

well as their relative rates under different steady-state test conditions, with insight into their relative rates clarified.

4.2 Experimental

The commercial monolith-supported Fe-zeolite SCR catalyst used in this study was supplied by GM. The sample was 1.5 in long and 0.9 in in diameter with a 400 cpsi cell density. Before testing, the catalyst was degreased in ambient air at 750°C for 4 h. It was wrapped with heat-expanding insulation material supplied by 3M and inserted into a horizontal quartz tube reactor, which was placed inside a Lindberg temperature-controlled electric furnace. The detailed experimental set-up is shown in Figure 1. Three thermocouples were inserted to monitor the upstream and catalyst front and back temperatures. During all experiments, temperature differences between the front and back were less than 4°C. For the spatial resolution set-up, a fused silica capillary was inserted into one of the cells in the radial center part of the catalyst for gas sampling. The position of the capillary was adjusted simply by pulling or pushing through a graphite ferrule seal at the reactor outlet. The outlet of the capillary was connected to a tee where dilution N₂ (240 ml/min) was mixed with the sampled gas. A MKS MultiGas 2030 FTIR analyzer was used, which has a 200 cm³ cell. The purpose of the N₂ dilution gas is to sweep this cell more frequently for speed of analysis as well as signal stability. NO, NO₂, N₂O, NH₃, H₂O and CO₂ were measured. The flow through the capillary was controlled by adjusting a valve close to the capillary outlet, to about 15 ml/min, with the average flow in each cell being 29 ml/min. The reactor pressure was kept slightly above 1 atm to force flow through the capillary. The CO₂ concentration was used to determine the flow rate in the capillary based on the dilution rate.

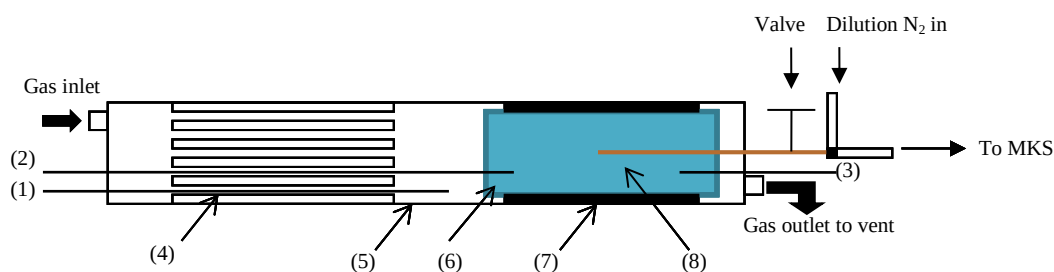


Figure 4.1 Experimental set-up. (1, 2, 3): thermocouples; (4) hollow quartz rods for gas preheating and distribution; (5) quartz tube reactor; (6) monolith Fe-zeolite catalyst; (7) insulation material; (8) fused silica capillary.

All the gases except balance N₂ were supplied by Praxair. Balance N₂ was produced using an On-Site N₂ generator. The gas flows were controlled with Bronkhorst mass flow controllers. All the upstream lines were heated and maintained at 120°C to prevent water condensation. Water was added via a Bronkhorst CEM system. In order to avoid reaction between NH₃ and NO₂ in the upstream tubing (formation of ammonium nitrate), NH₃ was introduced directly at the inlet of the quartz tube reactor rather than

upstream and pre-heated with the rest of the gases. Unless otherwise specified, the simulated exhaust gas contained 600 ppm of NO_x (NO+NO₂), 600 ppm NH₃, 8% O₂, 2.4 % H₂O, 5% CO₂ and balance N₂, and the total gas flow rate was 5.3 L/min, corresponding to a gas hourly space velocity (GHSV) of 28,000 h⁻¹. The system with capillary was tested to be inert to SCR reactions.

4.3 Results and discussion

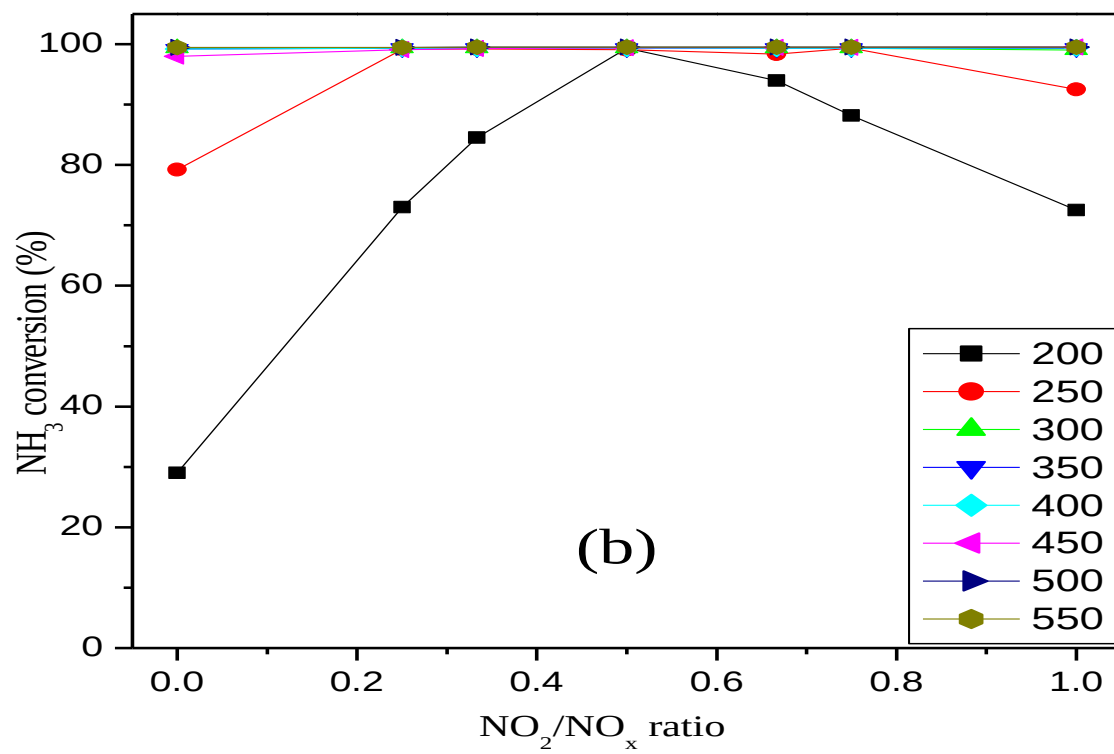
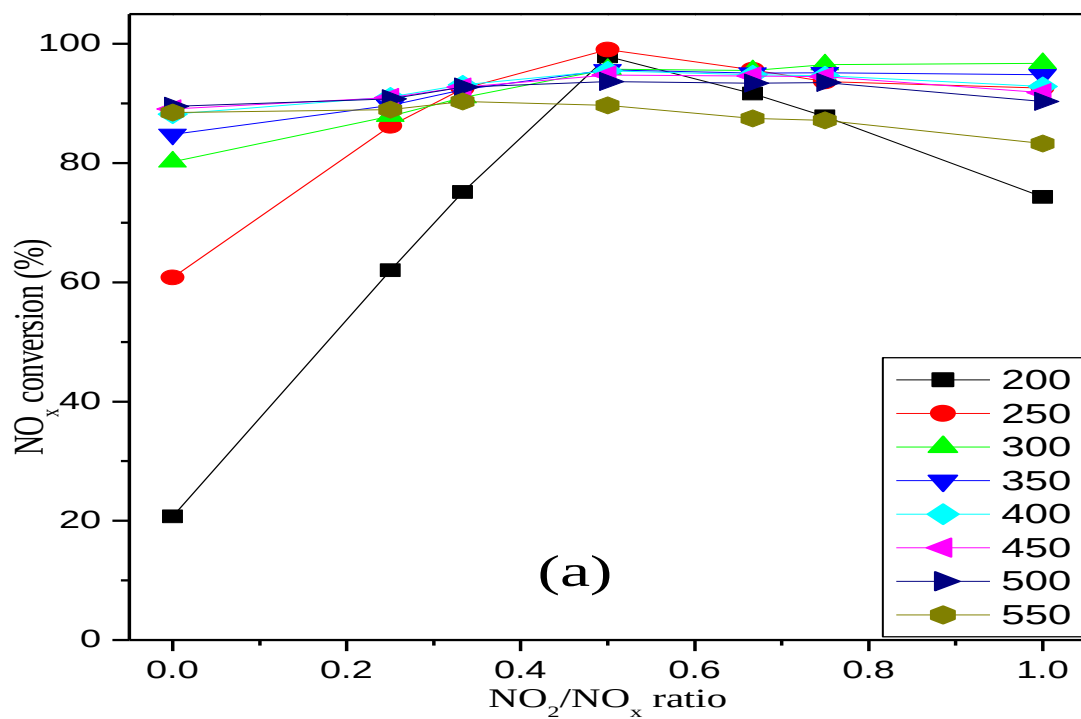
Error analyses for the results of this chapter and the following ones are included in the appendix.

4.3.1 Steady-state outlet concentration

The NO_x (a) and NH₃ (b) conversions, as well as the N₂O concentration (c), at the reactor outlet as a function of NO₂/NO_x ratio at different temperatures are shown in Figure 2. As shown in Figure 4.2 (a), NO_x conversion is very sensitive to the NO₂/NO_x ratio at temperatures between 250°C and 300°C, and a NO₂/NO_x ratio of 0.5, corresponding to an equimolar ratio of NO and NO₂, results in the highest conversion. This demonstrates that the fast SCR reaction does indeed have the highest rate at low temperatures. At higher temperatures (300~500°C), however, the dependence of NO_x conversion on NO:NO₂ ratio decreases, and very high NO_x conversion (generally around 90% or higher) can be achieved regardless of the NO_x feed. At the highest temperature tested, 550°C, the NO_x conversion actually decreased slightly when increasing the NO₂ ratio from 0.5 to 1. Based on the inlet NO_x ratios, the different SCR reaction types have different dependencies on temperature. For the standard SCR (NO₂/NO_x = 0), the conversion gradually increased with temperature from 250 to 400°C, and then remained about constant from 400 to 550°C. The fast SCR reaction (NO₂/NO_x = 0.5) conversion was consistently high, even at low temperatures, but decreased slightly at 500°C or higher. The conversion for NO₂-SCR (NO₂/NO_x = 1) first increased with increasing temperature until 300°C, and then decreased at higher temperatures.

The NH₃ conversion profiles are shown in Figure 4.2(b). They follow the same trend as NO_x conversion at low temperatures (200~250°C) but with slightly higher conversion, suggesting some of the NH₃ was already oxidized by O₂. At temperatures higher than 300°C, NH₃ was totally consumed, even without total NO_x conversion. Based on the N₂O outlet concentration profiles shown in Figure 2 (c), N₂O was only formed at NO₂/NO_x > 0.5 and increased with increasing NO₂ ratio, except at 200°C. At 200°C, a slight decrease in N₂O concentration was observed as the NO₂/NO_x ratio increased from 0.75 to 1, which is due to the decreased NO_x conversion. As a function of temperature, the N₂O concentration first increased from 200 to 250°C and then decreased, and none (less than 1ppm) is formed at 550°C.

Based on these results, the relative reaction rates of the three SCR reaction types are fast SCR > NO₂ SCR > standard SCR. However, the reaction details, such as whether they occur in series or in parallel and where these reactions occur along the monolith remain unknown. Spatially resolved gas concentration measurements were used to further characterize the three SCR reactions.



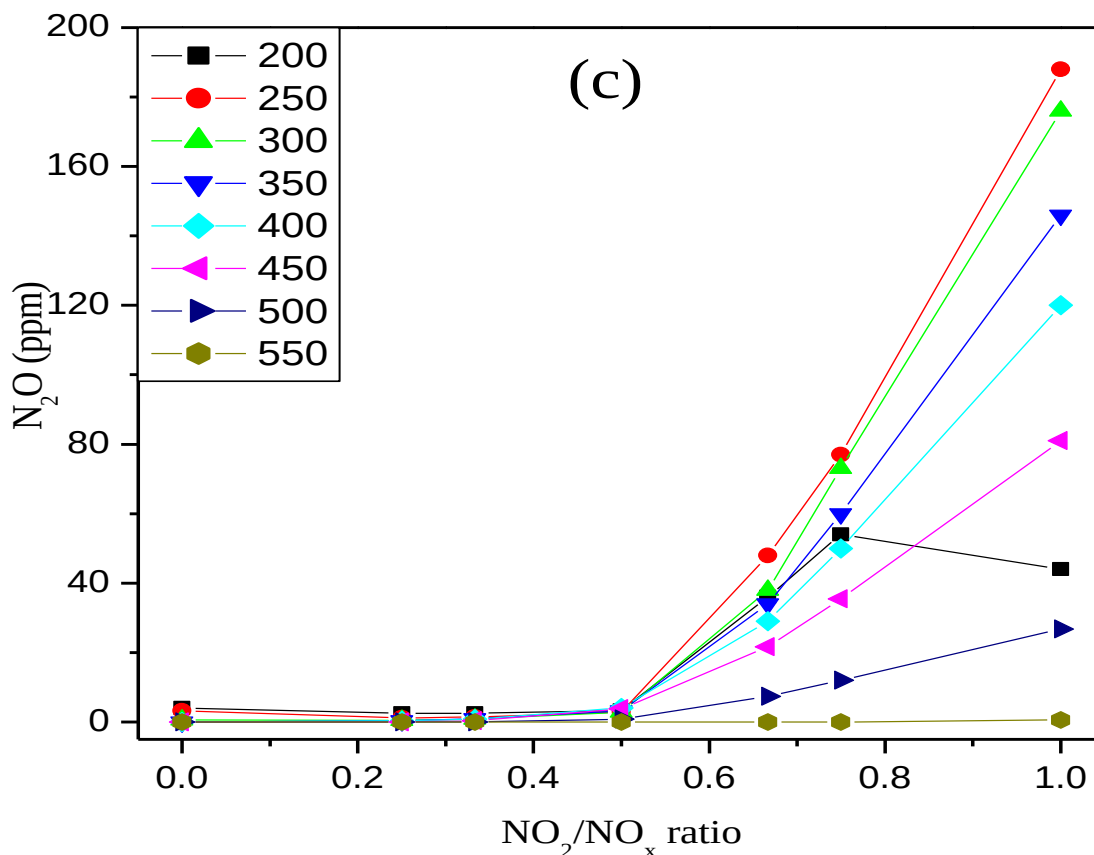


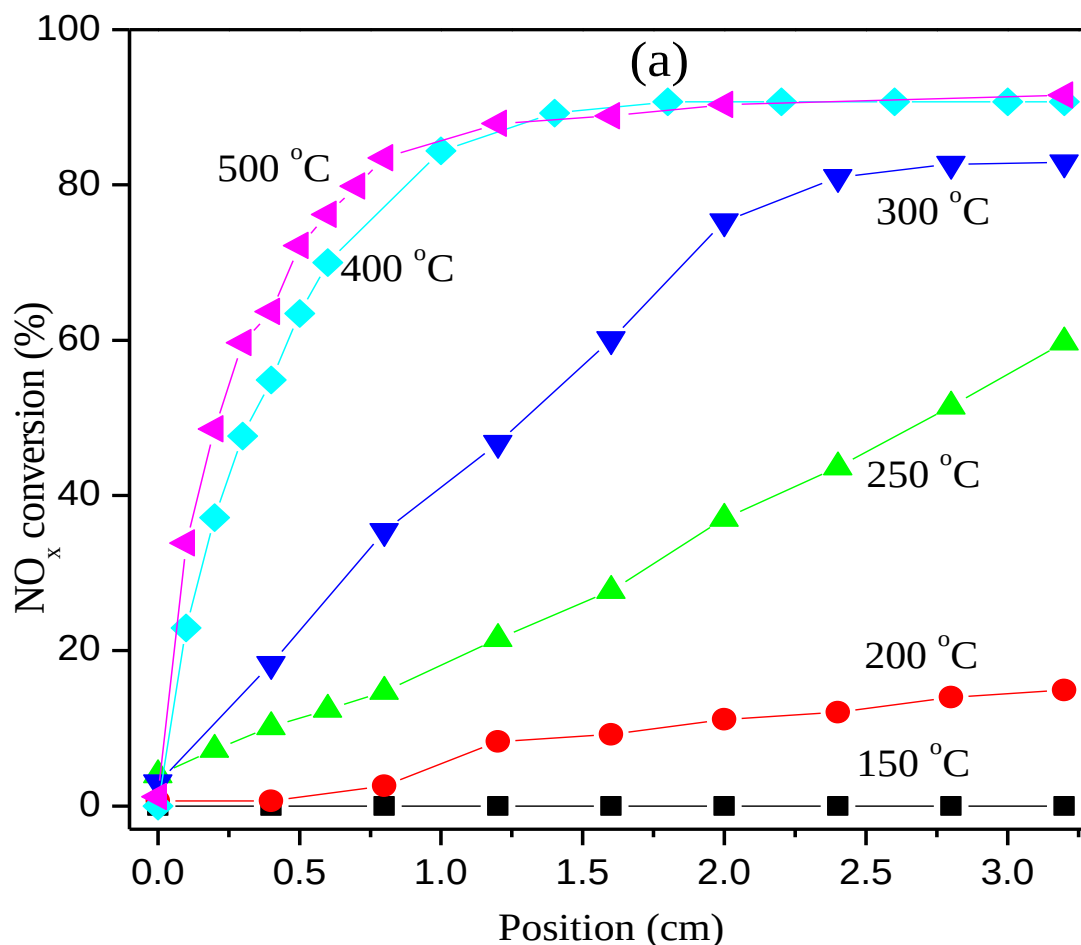
Figure 4.2 NO_x (a) and NH₃ (b) conversions and N₂O formation (c) as a function of NO₂/NO_x ratio at different temperatures. Feed gas composition: 600 ppm NO_x, 600 ppm NH₃, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.

4.3.2 Spatially resolved standard SCR

4.3.2.1 Spatially resolved standard SCR performance

The spatially-resolved gas concentration results for the standard SCR reaction, i.e. with only NO in the inlet gas feed, at different temperatures and positions along the length of catalyst are shown in Figure 3. As shown in Figure 4.3(a), there was no conversion at 150°C and some was observed at 200°C. Interestingly, at 200°C the reaction in the front 0.8 cm of catalyst was relatively small, with an inflection upwards after this position. This initial low activity is possibly due to NH₃ inhibition, which will be discussed later. At 250°C, NO_x conversion monotonically increased as a function of catalyst length, in a near linear trend. At 300°C, NO_x conversion first monotonically increased through the first 2.4 cm, then ended at about 80% conversion. At 400°C, SCR occurs only in the front 1.4 cm, but achieves about 90%

conversion. At 500°C the extent of SCR is only slightly increased, reaching a maximum conversion in the front 1.2 cm. The outlet NO_x conversions are similar at 400 and 500°C, and higher than that at 300°C. The NO_x and NH₃ concentration profiles at different temperatures and positions along the catalyst are shown in Figure 4.3 (b). It is clear that the reaction was quenched somewhere along the catalyst length above 300°C due to the complete consumption of the reductant NH₃. Theoretically, if the reaction occurs via standard SCR, 100% conversion can be obtained since the NO and NH₃ were introduced in the 1:1 stoichiometric ratio. But here the overconsumption of NH₃ occurs via oxidation by O₂. Therefore, there is competition between NO_x and O₂ for NH₃. Compared with 300°C, the higher NO_x conversions at 400 and 500°C indicate increased reactivity between the NH₃ and NO_x relative to O₂. So, although the oxidation of NH₃ by O₂ is of course also increased with increasing temperature (shown below), the reactivity of NO_x with NH₃ is increased to a greater extent.



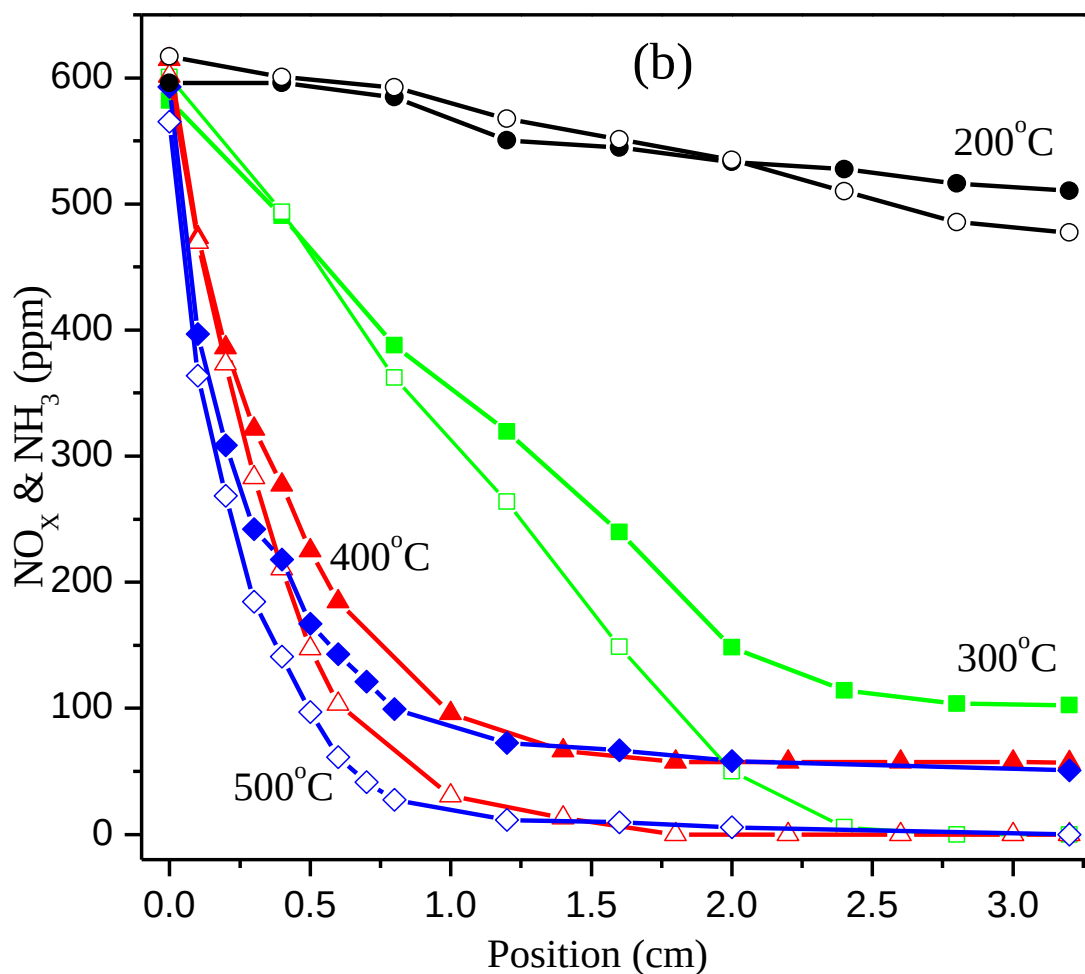


Figure 4.3 Spatial NO_x conversion (a), NO_x (solid) and NH₃ (hollow) concentrations, (b) profiles along the catalyst at different temperatures during standard SCR. Feed gas composition: 600 ppm NO, 600 ppm NH₃, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.

Experiments evaluating NH₃ oxidation by O₂ were performed. NH₃ oxidation by O₂ conversion as a function of temperature is shown in Figure 4.4. NH₃ oxidation by O₂ conversion slowly increased with increasing temperature from 200 to 400°C, and above 400°C a rapid increase in conversion was observed.

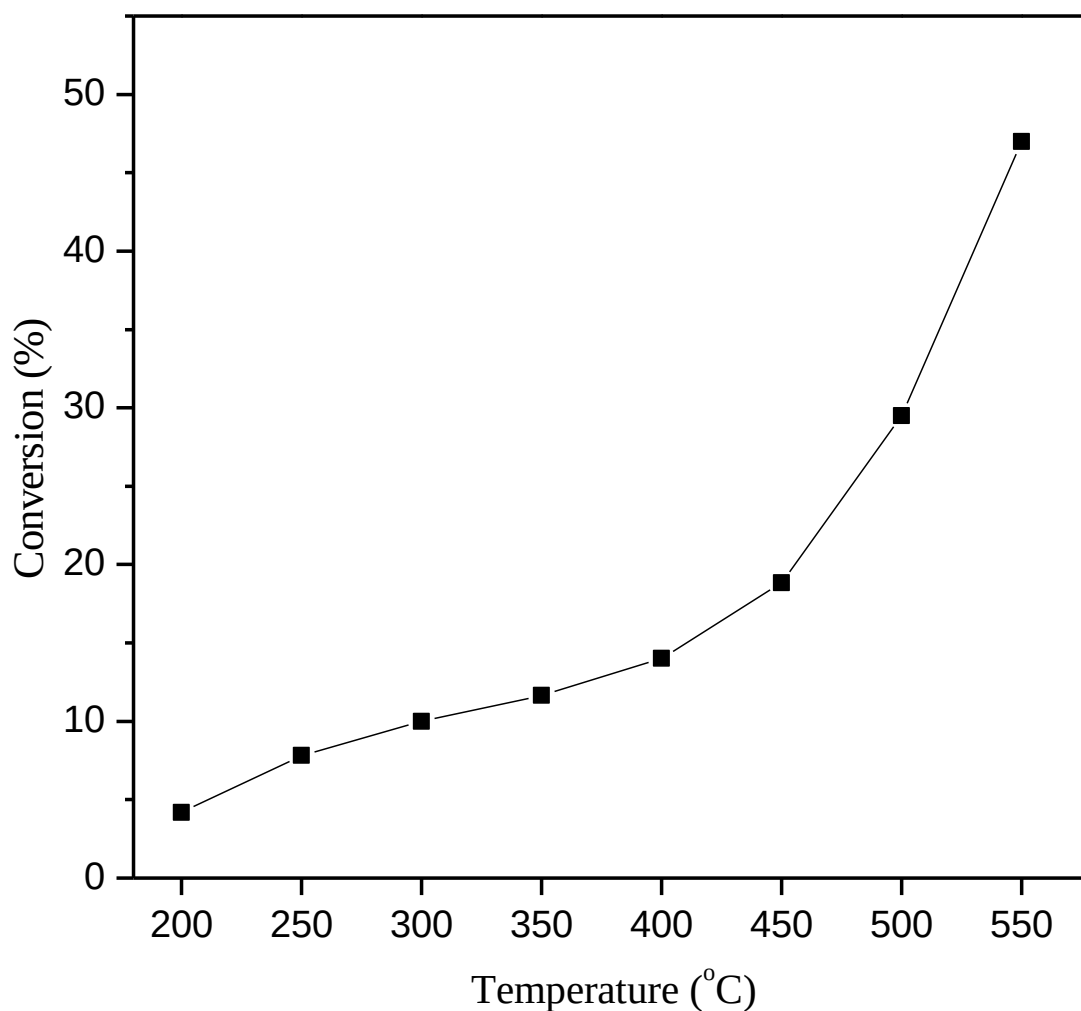


Figure 4.4 NH_3 conversion during its oxidation by O_2 at different temperatures. Feed gas composition: 600 ppm NH_3 , 2.4% H_2O , 5% CO_2 , 8% O_2 , balance N_2 ; GHSV = 28,000 h^{-1} .

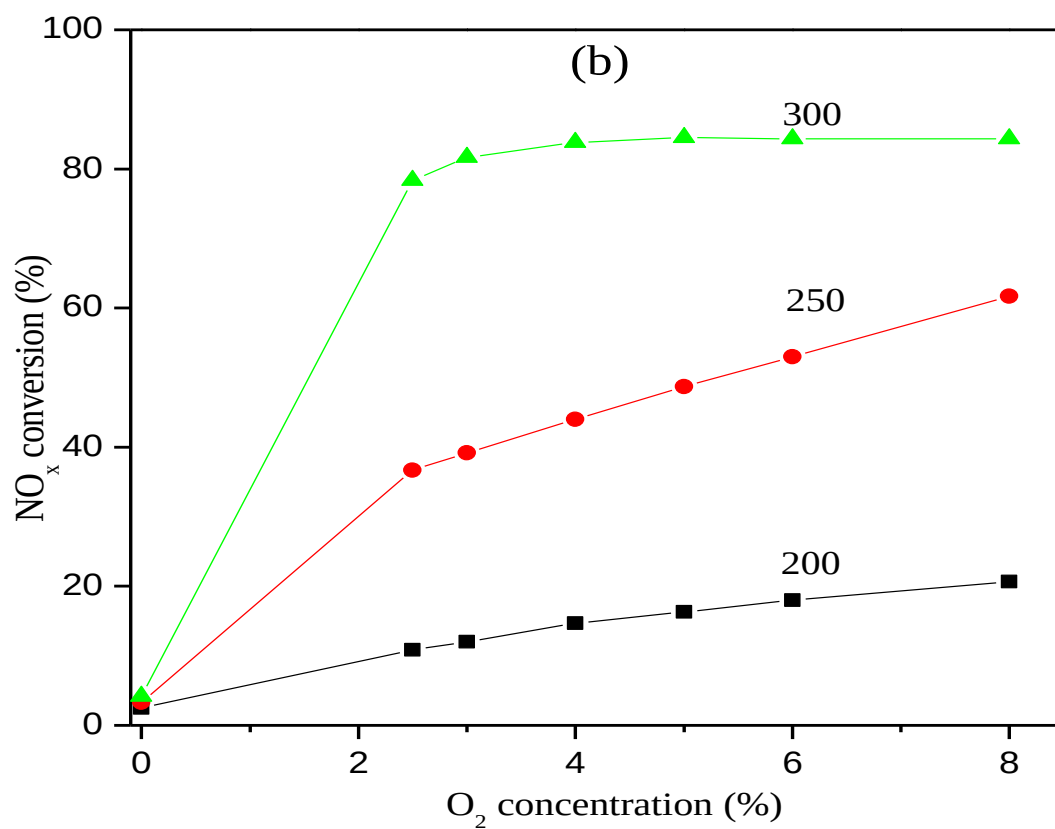
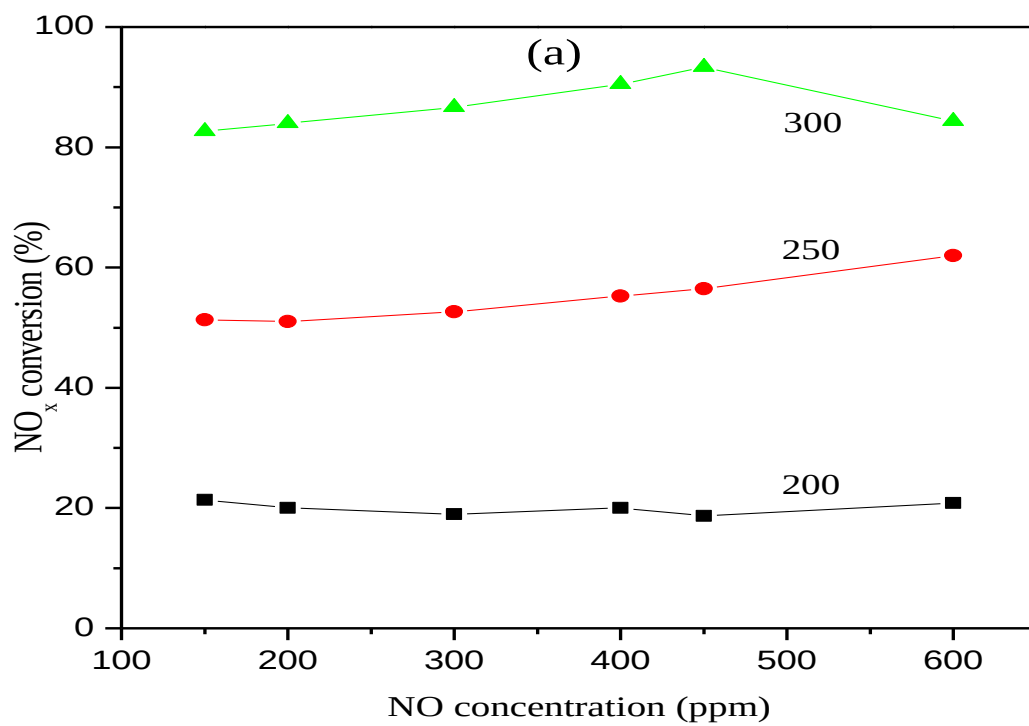
4.3.2.2 Reaction kinetics

Figure 4.5 (a) shows the effect of NO concentration, varied from 150 to 600 ppm, on the NOx conversion at 200, 250 and 300°C. The NH_3 and O_2 concentrations were fixed at 600 ppm and 8%, respectively. The effect of NO concentration on conversion differs between the temperatures. At 200°C, the NOx conversion remained at approximately 21%, regardless of the NOx concentration, suggesting that the reaction is 1st order with respect to NO. At 250°C, NOx conversion increased slightly with increasing NOx, whereas at 300°C, it first increased until NO = 450 ppm, then decreased with further increasing inlet NO concentration. As demonstrated in Figures 4.3b and Figure 4.4, the decreased conversion at 300°C under those conditions was due to insufficient reductant supply, since part of the NH_3 was oxidized

by O₂. However, the general increase in NO_x conversion with increasing NO concentration at temperatures higher than 250°C, as will be discussed in more detail later, is related to a decreased NH₃ inhibition effect.

The effect of O₂ concentration on NO_x conversion is shown in Figure 4.5(b). NO and NH₃ concentrations were both fixed at 600 ppm. NO_x conversion increased monotonically with increasing O₂ concentration at 200 and 250°C. Since the NO_x conversion at 300°C is very high and determined by the insufficient NH₃ supply, its dependence on O₂ was quite small. However, if there was no O₂ in the feed, even at 300°C, the reaction rate was very low, as would be expected based on the stoichiometry of reaction 1, with NO_x conversion close to zero.

The results of the effect of NH₃ concentration (from 150 to 1000 ppm) on NO_x conversion at different temperatures are shown in Figure 4.5(c). There is an optimum NH₃ concentration at each temperature that gives rise to a maximum in NO_x reduction. At low NH₃ input, such as 150 and 200 ppm, NH₃ is relatively insufficient and almost totally consumed at all temperatures investigated, with the corresponding NO_x conversions of 25% and 33%, respectively. This suggests that Fe-zeolite actually has excellent low temperature activity if there is no, or little, surface NH₃ coverage. However, with more NH₃ input, the NH₃ surface coverage is increasingly significant, and NO_x reduction decreases with increasing NH₃ giving rise to an observed NH₃ inhibition effect on NO_x reduction over this Fe-based SCR catalyst. It seems that the inhibition of NH₃ is mainly due to the adsorption of NH₃ on the active Fe sites, which may interfere with the adsorption properties (hindering access of NO_x molecules) [157] and/or the redox properties (the state of iron, Fe²⁺ vs Fe³⁺) [165], important for NO oxidation. It has been reported that the isolated Fe sites, or iron monomers, are primarily responsible for the standard SCR reaction [166], and are located at one exchange site in the zeolite framework. Therefore, each Fe²⁺ ion is partially charged (1+) and the charge is compensated by a OH group, which also acts as an adsorption site for NH₃ [167]. Such Fe-OH linkages have been detected by FT-IR techniques [168]. Different phenomena, however, have been observed on Cu-zeolites since Cu⁺ can be fully incorporated into the framework without an OH group for charge balance. Therefore, NH₃ has little, if any, effect on the catalytic performance of Cu-zeolite SCR catalysts since it cannot be adsorbed on the active copper sites [157, 167].



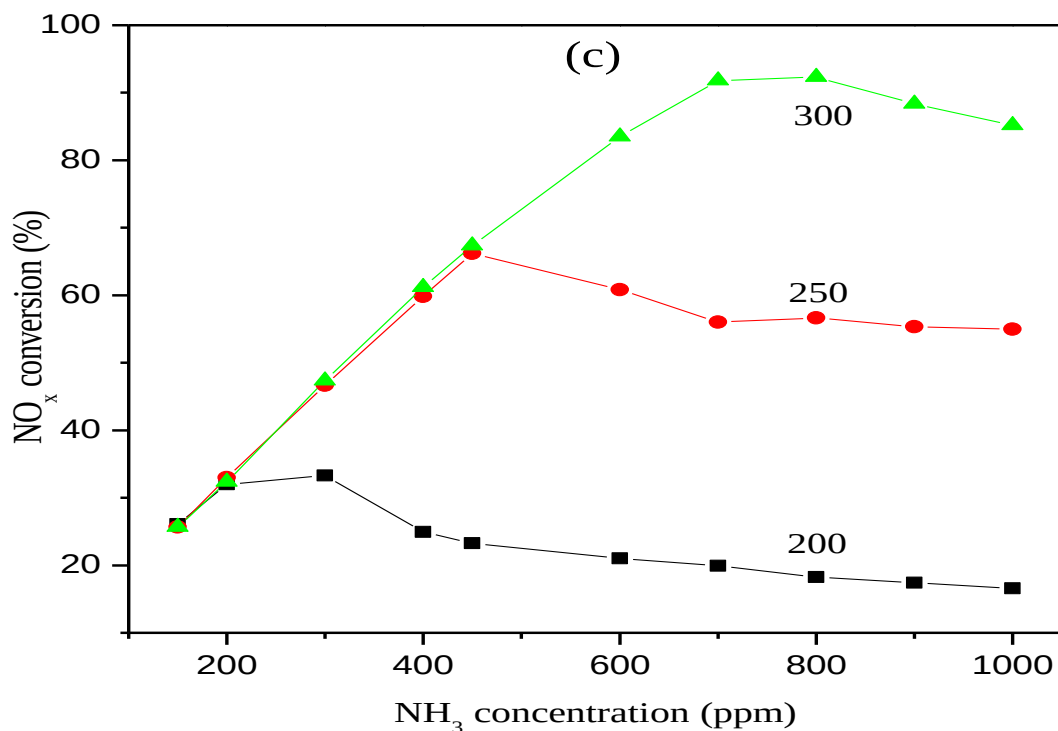


Figure 4.5 NO_x conversion as a function of (a) NO feed concentration (NH₃ = 600ppm, O₂ = 8%), (b) O₂ concentration (NH₃ = NO = 600 ppm), and (c) NH₃ concentration (NO = 600ppm, O₂ = 8%) at different temperatures; the balance gas composition was: 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.

For simplicity, the kinetics of the standard SCR reaction are expressed as a power-law rate equation: $r = k[\text{NO}]^{\alpha}[\text{O}_2]^{\beta}[\text{NH}_3]^{\gamma}$. Based on the results at 200°C, where the conversion was very low and mass-transfer limitations can be neglected, the reaction orders were calculated and the results are shown in Table 1. The reaction orders for NO and O₂ are 0.97 and 0.57, respectively, very close to first order and half order, consistent with results reported in literature [70, 169]; and the reaction order with respect to NH₃ is negative, -0.43, slightly lower than the reported value between -0.11 and -0.21 [70, 169], which is possibly due to the different range of NH₃ input. NO oxidation kinetics was also evaluated and the results are also shown in Table 1, as well as results with different NO concentrations in Figure 4.5. Reaction orders similar to those obtained for the standard SCR reaction were obtained for both NO and O₂, suggesting that NO oxidation is the critical step for standard SCR. This is consistent with previous findings showing that the oxidation activity of Fe-ZSM-5 is the main factor limiting high activity [166, 170]. As mentioned above, the negative order in NH₃ is due to the strong adsorption of NH₃ on the active Fe sites, which possibly influences NO adsorption and its subsequent oxidation.

Table 4.1 Reaction orders for NO oxidation and standard SCR at 200°C

Reaction	NO	O ₂	NH ₃
NO oxidation	1.00 (0.99)	0.57 (0.99)	n/a
standard SCR	0.97 (0.99)	0.56 (0.99)	-0.43 (0.99)

Concentration range: NO (150-600 ppm), O₂ (2.5%-8%), NH₃ (400-1000 ppm);

In parenthesis: coefficient of determination

It is worth noting that during NO oxidation (Figure 4.6), the NO_x conversion remains constant at each temperature for different NO concentrations, whereas from Figure 4.5(a), for the standard SCR reaction with different NO concentrations, the NO_x conversion only remained constant at 200°C, but increased with increasing NO concentration at 250 and 300°C. These differences are also the result of NH₃ inhibition. At low temperature, i.e. 200°C, the NO and NH₃ conversions are low, and the NH₃ concentration in the gas phase does not change much with increasing NO. In other words, the surface NH₃ coverage on the active Fe sites remained nearly constant, and therefore, the NO oxidation rate was unchanged and a constant conversion was observed. However, at higher temperature, i.e. at 250 and 300°C, NO_x and NH₃ consumption was significant, with conversions higher than 50%. Therefore, the NH₃ concentration is sensitive to the input NO_x. Higher NO_x input consumes more NH₃ and weakens its negative impact, thus higher conversion can be achieved via the higher NO oxidation rates due to more exposed active sites. However, at 300°C, a decrease in NO_x conversion was observed as the NO_x concentration was increased from 450 to 600 ppm. This can be attributed to insufficient NH₃ supply, as demonstrated by the spatial resolution results.

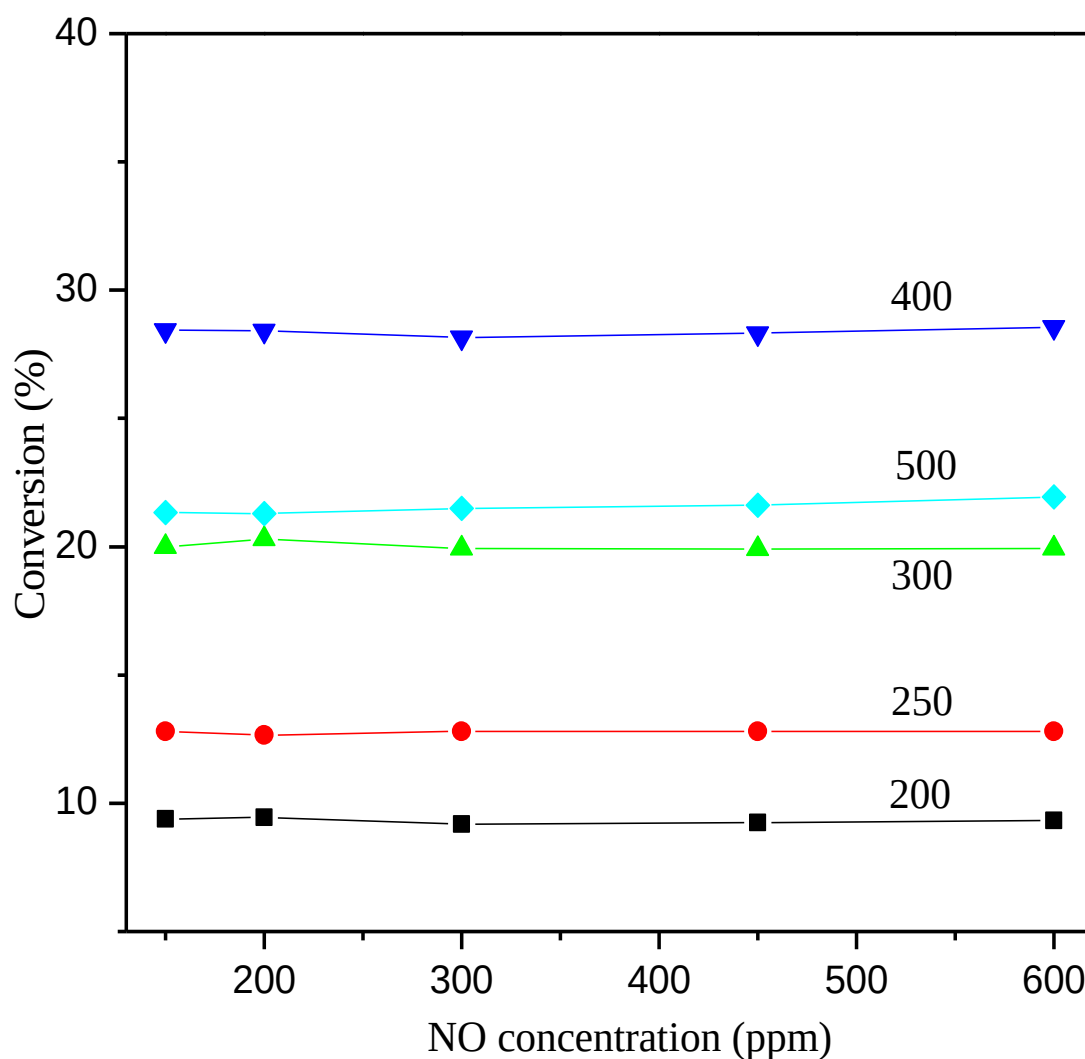


Figure 4.6 NO oxidation conversion as a function of NO concentration at different temperatures. Feed gas composition: 0 – 600 ppm NO, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.

4.3.2.3 Spatially resolved NO oxidation

Since NO oxidation seems to be a critical step in the standard SCR reaction, this reaction was further investigated. The overall outlet conversion at different NO concentrations and different temperatures is shown in Figure 4.5. The NO conversion increased from 200 to 400°C, and then decreased from 400 to 500°C. The reason that the highest NO conversion being achieved at 400°C is due to NO oxidation being kinetically limited at lower temperatures and thermodynamically limited at higher temperatures. Spatially-resolved NO₂ concentrations along the catalyst at different temperatures were measured, and the results are shown in Figure 6. The NO₂ concentration monotonically increased along the catalyst between

200 and 400°C, and at 500°C first increased and then kept constant due to thermodynamic limitations. Worth noting is that NO oxidation significantly increased as the temperature was increased from 300 to 400°C. This helps explain the performance of the standard SCR reaction, as shown in Figure 4.3(a). The catalyst length used to achieve 80% conversion decreased from 2.4 cm at 300°C to less than 1 cm at 400°C. Also, because of the much higher NO oxidation rate at 400°C compared to that at 300°C, a higher selectivity of NH_3 reacting with NOx, via the fast SCR reaction, rather than with O_2 occurs, and a higher outlet NOx conversion can therefore be achieved. In comparing the SCR performance at 400 and 500°C, however, the differences were quite small. The same NOx conversion was achieved at around 1.2 cm catalyst length as shown in Figure 4.3(a), and the differences in NO_2 concentrations at 1.2 cm, as shown in Figure 4.8, were also quite small. Therefore, these results consistently suggest that NO reduction by NH_3 is closely related to NO oxidation.

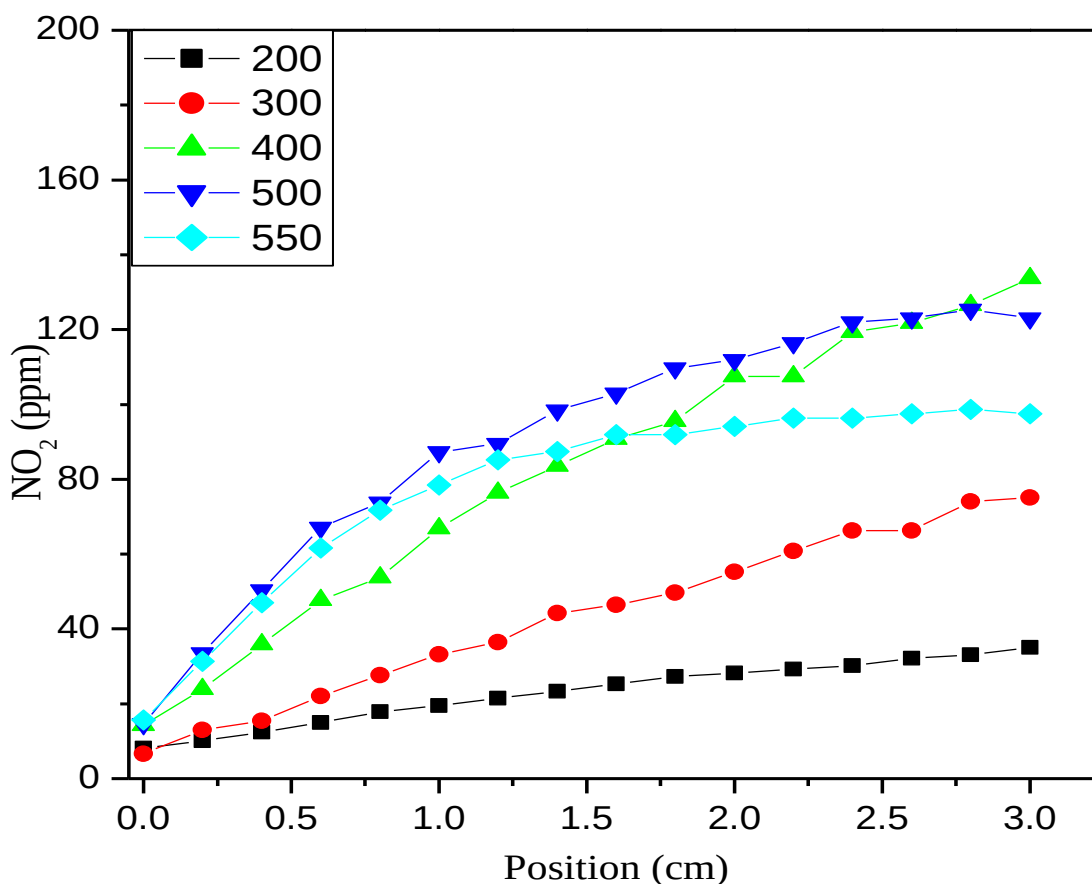


Figure 4.7 Spatial NO_2 concentration profiles during NO oxidation at different temperatures. Feed gas composition: 600 ppm NO, 8% O_2 , 2.4% H_2O , 5% CO_2 , balance N_2 ; GHSV = 28,000 h^{-1} .

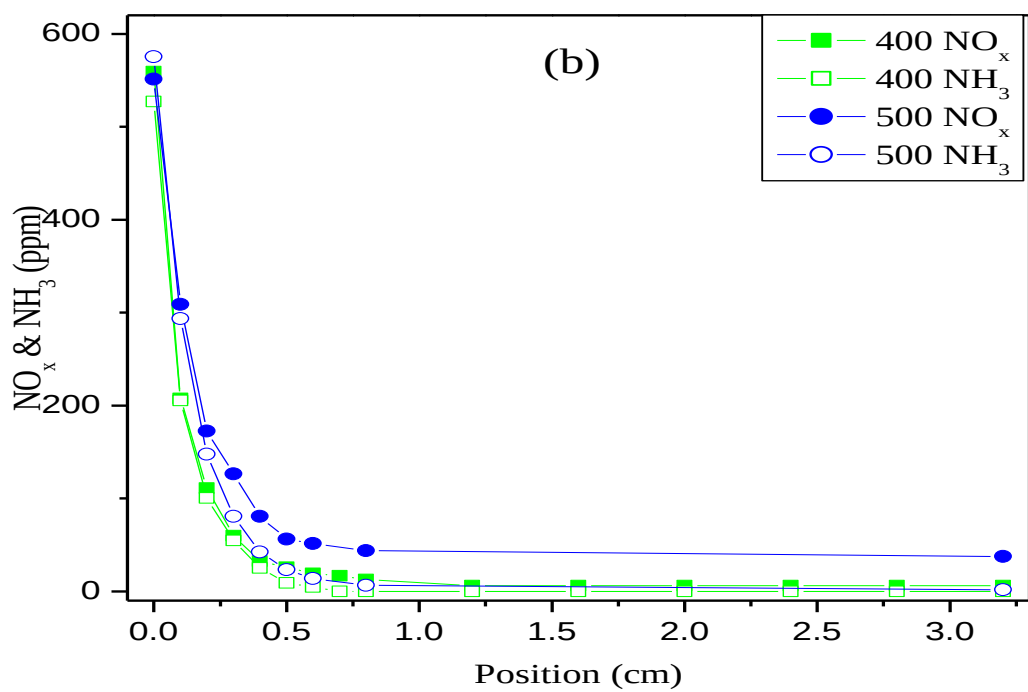
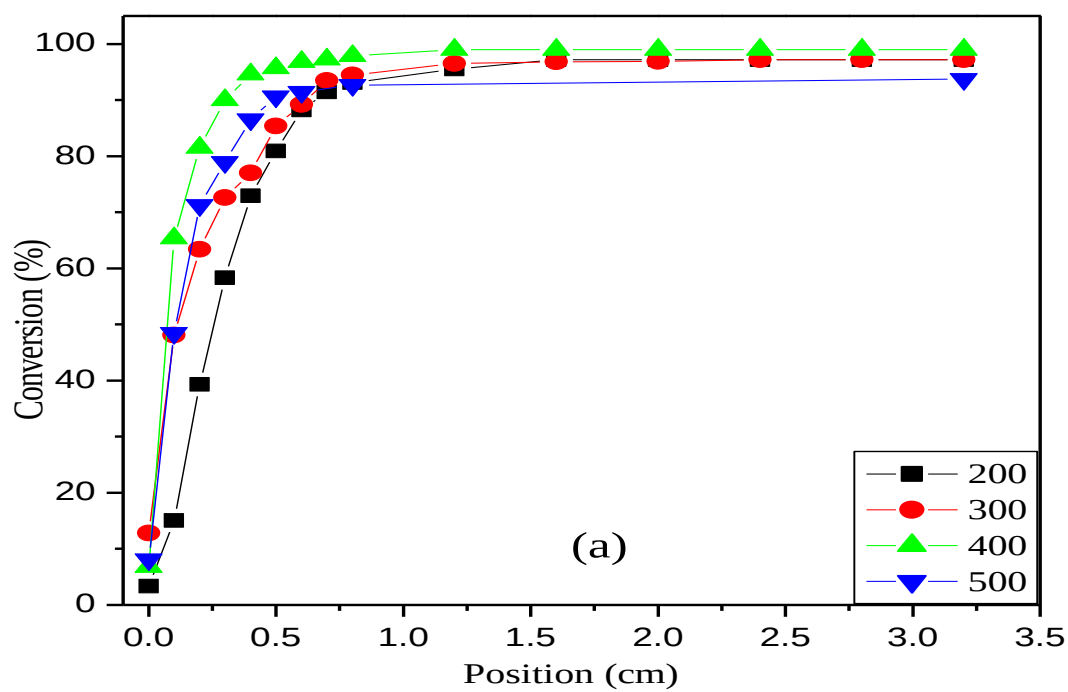


Figure 4.8 Spatial NO_x conversion (a), NO_x and NH₃ concentrations, (b) profiles along the catalyst at different temperatures during fast SCR. Feed gas composition: 300 ppm NO, 300 ppm NO₂, 600 ppm NH₃, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.

In summary, based on the kinetic study and spatial resolution results, NO oxidation over the Fe sites is the rate-determining step for the standard SCR reaction over this Fe-zeolite catalyst. NH_3 , when present in large amounts, has an inhibition effect on the standard SCR reaction because of its strong adsorption on Fe sites, which suppresses NO oxidation. At 300°C, under the conditions tested, the standard SCR reaction is limited by an insufficient NH_3 supply but not the reaction kinetics, since at this temperature NO oxidation is relatively slow, making the reaction proceed over a long catalyst length (front 2.4 cm), which increases the probability of NH_3 oxidation by O_2 . As compared to 300°C, the higher conversions at 400 and 500°C, are due to significantly greater NO oxidation extents, which results in NOx being more competitive with O_2 for reductant NH_3 , leading to the decreased amount of catalyst used and increased NOx conversion.

4.3.3 Spatial resolution of fast SCR

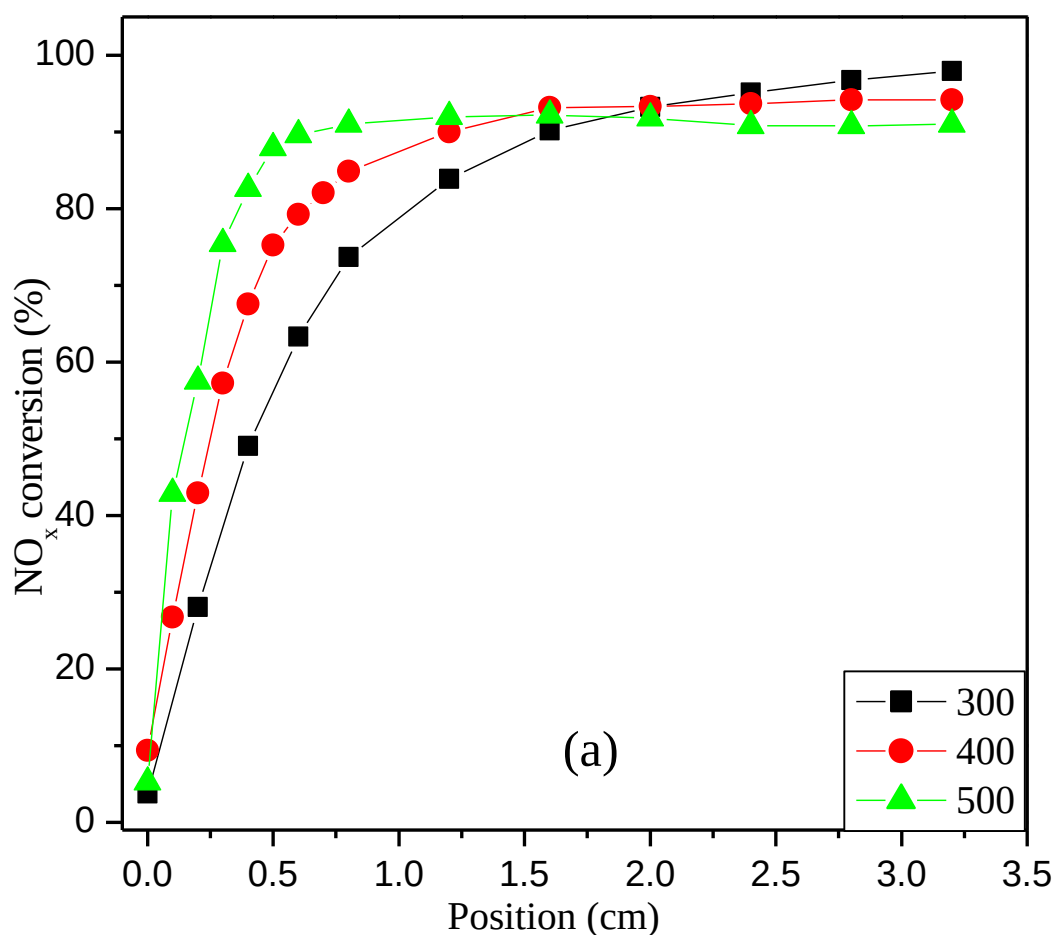
In real application, in order to enhance the low temperature performance, an upstream DOC is generally installed, and therefore, the feed gas in front of the SCR catalyst consists of a mixture of NO and NO_2 . The spatially resolved gas concentration results for the fast SCR reaction ($\text{NO}_2/\text{NOx} = 0.5$) at different temperatures are shown in Figure 4.8. Very high NOx conversion was achieved over a very short length of catalyst. For example, NOx conversion greater than 90% was achieved in the front 0.8 cm of the catalyst at all temperatures investigated, as shown in Figure 4.8(a). Although the reaction rate dependence on temperature is much smaller for fast SCR compared to standard SCR, the reaction was slowest at 200°C and fastest at 400°C. Between 200 and 400°C, very high NOx conversions (>95%) were obtained, suggesting that the selectivity between NH_3 and NOx is very high, much higher than for that with NO in the standard SCR reaction. At 500°C the outlet NOx conversion was slightly decreased due to some NH_3 oxidation by O_2 at high temperature, which is confirmed by the NOx and NH_3 concentration profiles as a function of catalyst length, as shown in Figure 4.8(b). Note, there is some conversion observed even at the catalyst front (zero position), which is possibly due to some slight gas-phase reaction within the tube reactor since the reaction between NO_2 and NH_3 can occur without catalyst in the presence of H_2O . This reaction can be confirmed by the formation of white powder NH_4NO_3 inside the front tube if NO_2 , NH_3 and H_2O were introduced at the same time, for long enough time periods.

4.3.4 Spatial resolution of NO_2 -SCR

The spatially-resolved gas concentration results for NO_2 -SCR at different temperatures are shown in Figure 4.9. Compared with the other two SCR reactions, as shown in Figure 4.2 (a), NO_2 -SCR is slower than fast SCR but faster than standard SCR. High conversion (>90%) was obtained from 300 to 500°C. This suggests that the reaction between NO_2 and NH_3 does not occur solely through reaction (4.3), namely NO_2 -SCR to N_2 , where the theoretical maximum NOx conversion is only 75%. It is likely that the NO_2 - NH_3 reaction also occurs through NO_2 -SCR to N_2O with equimolar consumption of NH_3 and NO_2 .

Significant N_2O formation supports this path. As shown in Figure 4.2(c), the N_2O outlet concentration decreases with increasing temperature above 250°C .

N_2O concentrations as a function of catalyst position are plotted in Figure 4.9 (b). At 300 and 400°C , N_2O was readily formed, and then kept relatively constant. However, at 500°C , the N_2O concentration first increased to about 60 ppm in the front 0.6 cm, but then slowly decreased, indicating that the N_2O formed in the front of the catalyst decomposes at the back. This is consistent with previous results showing that N_2O starts to decompose on Fe-ZSM-5 at 450°C [94]. On this basis, N_2O decomposition at high temperatures is at least one of the reasons for the observed decrease in N_2O concentration with increasing temperature.



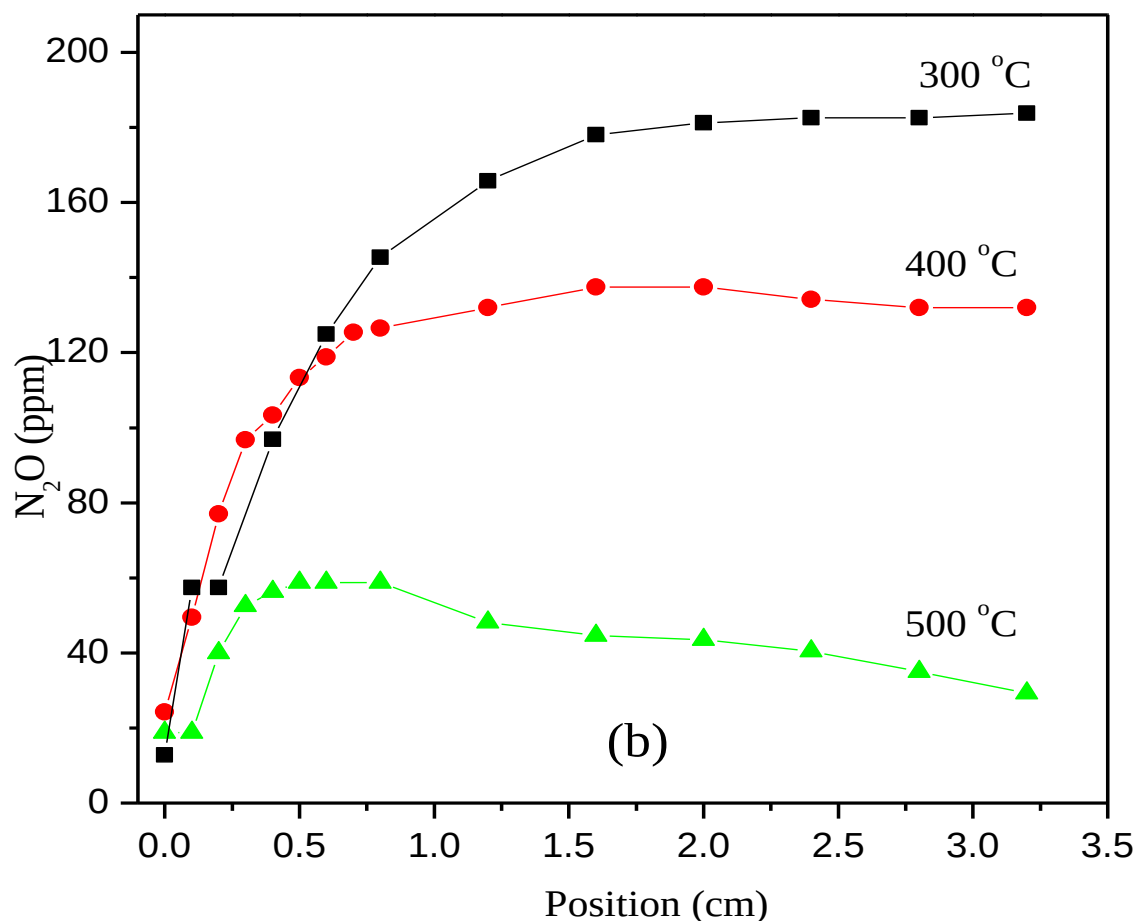


Figure 4.9 Spatial NO_x conversion (a), N₂O concentration (b) profiles along the catalyst at different temperatures during NO₂-SCR. Feed gas composition: 600 ppm NO₂, 600 ppm NH₃, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.

Another contributing factor for decreased N₂O formation with increasing temperature could be an increase in the NO₂-SCR to N₂ relative to the NO₂-SCR to N₂O reaction. The extent of NO₂-SCR to N₂ can be inferred by comparing NO_x conversions at 550°C. Based on the data shown in Figure 5.2, NO_x conversion with pure NO₂ as the NO_x source at 550°C, around 80%, is lower than that observed under standard SCR conditions, where with pure NO as the NO_x source, around 90% was achieved. It would be expected that less NH₃ is oxidized by O₂ using NO₂ as the NO_x source due to its higher reactivity, and therefore more NH₃ reacts with NO₂, compared with NO in the standard SCR reaction. This therefore suggests that NO₂-SCR to N₂ at 550°C is the more dominant pathway, with the 80% conversion close to the theoretical 75% value if an equimolar amount of NO₂ and NH₃ is introduced. Furthermore, at temperatures above 450°C, with increasing relative NO₂ (NO₂/NO_x > 0.5) in the feed gas, the NO_x

conversion tends to decrease, indicating that increased NO₂-SCR to N₂ occurs, which decreases the overall NO_x conversion due to “extra” NH₃ consumption.

However, at temperatures between 300 and 400°C, NO₂ and NH₃ consumption was approximately 1:1, indicating that the reaction mainly occurred through reaction (4.4) and/or (4.5). In general, it has been well-accepted that the formation of N₂O, as shown in reaction (4.5), occurs through the decomposition of NH₄NO₃, formed in reaction (4.4), and NH₄NO₃ reportedly will decompose at temperatures above 250°C [171]. Here the question is whether all the NH₄NO₃ would selectively decompose into equimolar N₂O and N₂, as shown by the reaction path (4.5). From Figure 4.2, the conversion is greater than 90% between 300 and 400°C with only NO₂ as the inlet NO_x source, which means that more than 270 ppm N₂O should have formed if only via reaction (4.5). However, the maximum N₂O concentration obtained was 188 ppm. Decreased N₂O formation should not be related to its thermal decomposition due to the relatively low temperature. This quantitative analysis suggests that other reaction routes occur between 300 and 400°C. Literature evidence shows though that NH₄NO₃ does not decompose to only N₂O, but includes dissociation into NH₃ and HNO₃, and decomposition into N₂ and O₂ [171, 52]. Here the most probable route would be its dissociation into NH₃ and HNO₃, as shown in reaction (4.7). It has been reported that if NO is present, the formed HNO₃ can be reduced to NO₂ [171]; if NO is absent, HNO₃ will thermally decompose into NO₂ and O₂ as shown in reaction (4.8), especially at high temperature. If we assume that no HNO₃ is available or is stable at temperatures higher than 300°C, by combining reactions (4.4), (4.7) and (4.8), overall reaction (4.9) develops, which explains the decreased N₂O formation.



Finally, another possibility for decreased N₂O formation is via the following reaction route. First, NO₂ decomposes into NO and O₂, and then the decomposed NO reacts very quickly with NO₂ and NH₃ via the fast-SCR reaction. NO₂ decomposition experiments were carried out, and outlet NO concentrations of 13, 134 and 140 ppm were detected with 600 ppm NO₂ in the feed at 300, 400 and 500°C, respectively. However, even despite the different reaction route, the overall reaction equation is still the same as (4.9), with the consumption of equimolar NH₃/NO₂ and formation of N₂ only. The co-occurrence of reaction (4.9), besides NO₂-SCR to N₂O with equimolar formation of N₂ and N₂O, is also supported by the much higher amount of N₂ formed relative to N₂O, as detected by MS, over a Fe-zeolite catalyst with NO₂ as the feed NO_x between 150 to 400°C [95].

In summary, for NO₂-SCR with equimolar NH₃ and NO₂ fed, significant amounts of N₂O form. However, its formation decreases with increasing temperature beyond 250°C. Decomposition of N₂O at the back of the catalyst, increased NO₂-SCR to N₂ (3) at high temperature, the increasing relevance of reaction route

(9), resulting from successive decomposition of NH_4NO_3 to NH_3 and HNO_3 , then HNO_3 to NO_2 and O_2 , and possibly NO_2 decomposition to NO and O_2 , contribute to decreased N_2O formation.

4.3.5 Spatial resolution of SCR with different NO_2 feed concentrations

In real application, depending on driving conditions and the upstream DOC's performance, NO_2 concentrations will fluctuate. In order to figure out the reaction patterns and the length of catalyst used for different NO_2 levels, NO_x conversion with different NO_2/NO_x ratios were measured at 300°C , and the results are shown in Figure 4.10. These data clearly demonstrate that the relative reaction rates follow; standard SCR < SCR with pure NO_2 < fast SCR. The catalyst lengths used to achieve 80% NO_x conversion for the three types of reaction are 2.4 cm, 1.2 cm and 0.5 cm, respectively. Alternatively, at the 0.8 cm position, the NO_x conversion values for these three reactions are 35%, 74% and 94%, respectively.

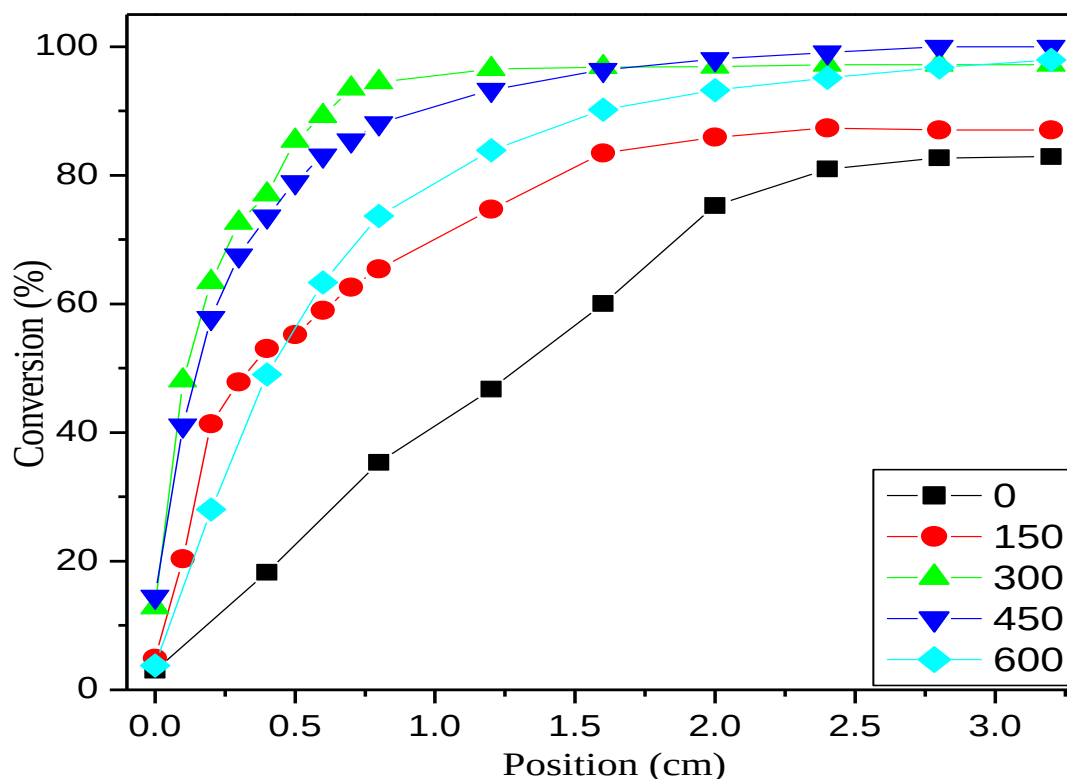
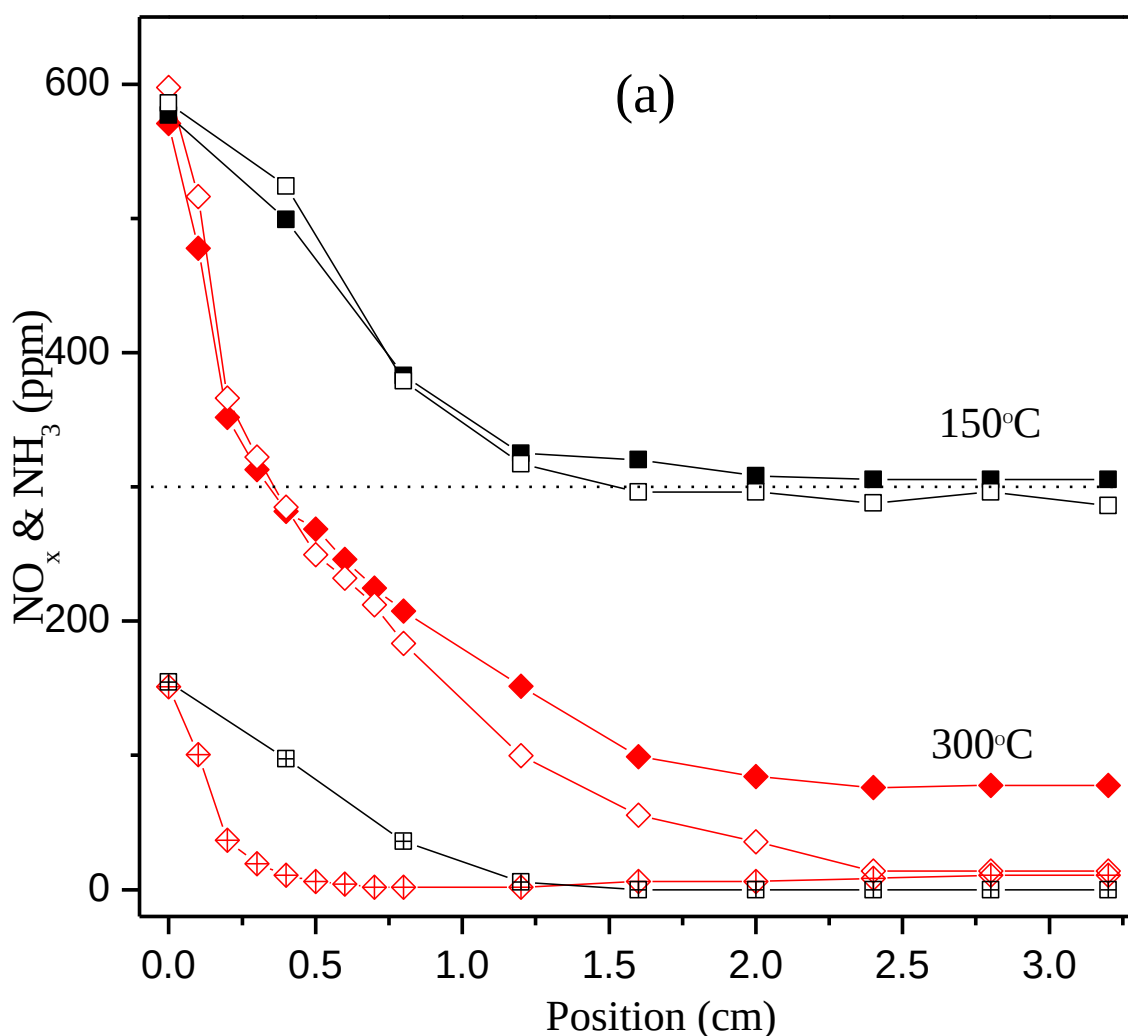


Figure 4.10 Spatial NO_x conversion along the catalyst at 300°C with different NO_2 feed concentrations. Feed gas composition: 600 ppm NO_x (NO_2 : 0 – 600 ppm), 600 ppm NH_3 , 8% O_2 , 2.4% H_2O , 5% CO_2 , balance N_2 ; GHSV = $28,000 \text{ h}^{-1}$.

For the case with 450 ppm NO and 150 ppm NO_2 , the reaction occurs very fast in the front 0.4 cm, higher than SCR with pure NO_2 , and then the reaction slows and ceases at about 2.0 cm. The NO_x , NH_3 and NO_2

profiles for this reaction at 300°C are shown in Figure 4.11(a) and the consumption of each species along the catalyst (the concentration differences from zero position) are shown in Figure 4.11(b). These results demonstrate that in the first 0.4 cm, only the fast reaction occurs, since NO and NO₂ are consumed exactly in a 1:1 ratio. After that, standard SCR proceeds, and at a slower rate, from 0.4 to 2.4 cm until all the NH₃ is consumed, then NO_x reduction stops. Based on these results, the fast and standard SCR reactions proceed in series, not in parallel. The reaction with the same feed was also investigated at 150°C, and the NO_x, NH₃ and NO₂ profiles are shown in Figure 4.11 (a). Here, only the fast reaction occurred in the first front 1.6 cm, and then the reaction stopped since the catalyst is not active toward the standard SCR reaction at this low temperature, consistent with the results in Figure 3.



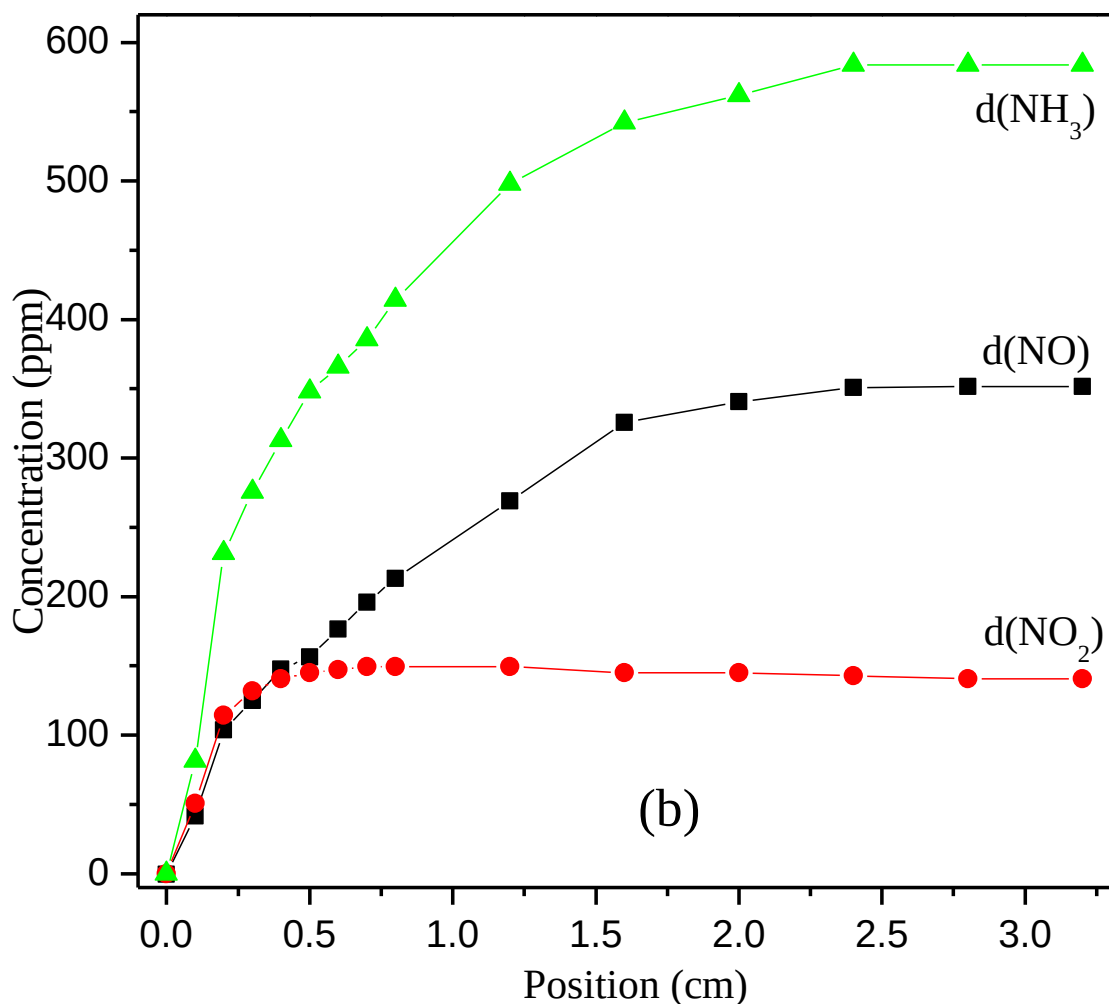


Figure 4.11 (a) Spatially-resolved NO_x(solid), NH₃(hollow) and NO₂(cross) concentration profiles at 150°C (black) and 300°C (red); and (b) NH₃, NO and NO₂ consumption profiles along the catalyst at 300°C. Feed gas composition: 450 ppm NO, 150 ppm NO₂, 600 ppm NH₃, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.

Different behaviour was observed for the case with 150 ppm NO and 450 ppm NO₂. The NO_x and NH₃ concentration profiles are shown in Figure 4.12(a) and the consumption of each species along the catalyst is shown in Figure 4.12(b). Again note, some gas-phase reaction between NH₃ and NO₂ occurs by the front of the catalyst, which consumes about 90 ppm of both NH₃ and NO₂, as shown in Figure 4.12(a), since only 510 ppm NO_x and NH₃ are observed at the zero position. From Figure 4.12(b), more NO₂ is consumed than NO, and increasing N₂O production (data not shown) was observed in the front 0.8 cm,

where NO is also totally consumed. This demonstrates that NO_2 -SCR and the fast SCR reactions proceed in parallel.

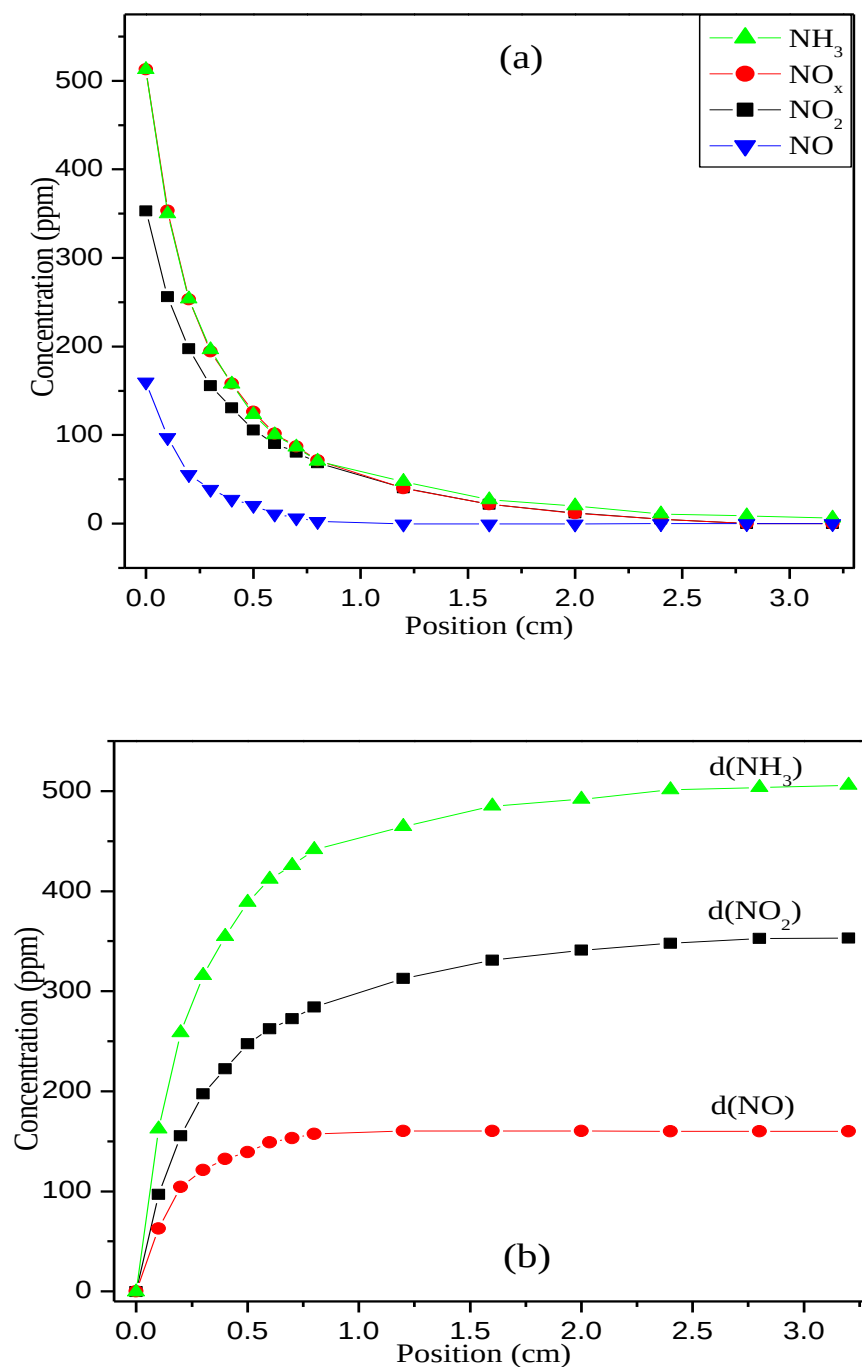


Figure 4.12 (a) Spatially-resolved NO_x , NH_3 and NO and NO_2 concentration profiles at 300°C; and (b) NH_3 , NO and NO_2 consumption profiles along the catalyst. Feed gas composition: 150 ppm NO, 450 ppm NO_2 , 600 ppm NH_3 , 8% O_2 , 2.4% H_2O , 5% CO_2 , balance N_2 ; GHSV = 28,000 h^{-1} .

The different reaction patterns, in series or in parallel, with respect to different NO_2 levels, can be rationalized by the relative rates between fast SCR, standard SCR and SCR with pure NO_2 . In summary, the reaction patterns at 300°C are determined by the NO_2/NO_x ratio in the feed gas. If $\text{NO}_2/\text{NO}_x < 0.5$, as in the case with 450 ppm NO and 150 ppm NO_2 , the reactions proceed in series, namely first the fast SCR reaction followed by standard SCR. If $\text{NO}_2/\text{NO}_x > 0.5$, as in the case with 150 ppm NO and 450 ppm NO_2 , the reactions proceed in parallel, with fast SCR and NO_2 SCR occurring at the same time at the front of the catalyst.

4.4 Conclusions

Standard SCR, fast SCR and SCR with pure NO_2 can proceed at significantly different rates especially at 300°C or below, and can be correlated to the amount of catalyst used. The catalyst lengths used to achieve 80% conversion at 300°C were around 2.4, 1.2 and 0.5 cm, for the standard SCR, SCR with pure NO_2 and fast SCR reactions, respectively, under the conditions used.

Standard SCR performance is closely related to NO oxidation over active Fe sites. The reaction orders with respect to NO and O_2 are very close to 1 and 0.5 for both the standard SCR reaction and NO oxidation over the Fe zeolite catalyst tested. However, NH_3 has an inhibiting effect on the standard SCR reaction since it can competitively adsorb on the same active sites that participate in NO adsorption and oxidation. For standard SCR at 300°C or higher, the overall conversion was limited by insufficient NH_3 supply since part of the NH_3 is oxidized by O_2 and equimolar amounts of NH_3 and NO were added. Increasing the temperature past 300°C results in more significant NO_x reduction since NO oxidation significantly increases, which also increases the selectivity of NH_3 reacting with NO_x rather than O_2 .

NO_2 -SCR with equimolar NH_3 and NO_2 feed results in significant N_2O production, and N_2O formation tends to decrease with increasing temperature above 250°C . At temperatures between 300 to 400°C , besides the N_2O formation route, other reactions contribute to decreased N_2O formation, including the decomposition of NH_4NO_3 into HNO_3 then to NO_2 and O_2 , and/or NO_2 decomposition into NO and O_2 . At high temperatures, both the enhanced NO_2 -SCR to N_2 and N_2O decomposition at the back part of the catalyst contribute to decreased N_2O formation as well.

Different reaction patterns were observed for unbalanced $\text{NO}:\text{NO}_2$ ratios ($\neq 1$) at 300°C . At ratios larger than 1, the reaction proceeded in series, namely via fast SCR reaction first, followed by standard SCR. Otherwise, the reactions proceeded in parallel, with fast SCR and NO_2 -SCR occurring at the same time, beginning at the very front of the catalyst. The different patterns are determined by the relative reaction rates of the three types of SCR reaction.

This bulk of this chapter was published in 2011, SAE Technical Paper Series, 2011-01-1138. Chapter numbers have been inserted to help the reader, and Figure numbers changed to reflect the chapter number. Again, there is redundancy to the thesis in the introduction and experimental methods sections.

Chapter 5 Cu-Zeolite SCR Catalyst Thermal Deactivation Studied with FTIR Spatial Resolution

5.1 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 [175]. 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 [176-177]. In addition, an emerging technology being developed involves depositing the SCR catalyst onto the conventional wall-flow particulate filter [178]. 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 [99-101, 104, 108-109, 177, 179-181]. 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 [108] found that deactivation of zeolite-based cobalt and palladium catalysts are in part caused by temperature-induced ion migration. Grinsted et al [109] 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 [109, 182, 112]. 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 [112], 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 [113] 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 [182], 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 [142-143]. 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 [145]. 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 [143-144] has also been used to monitor competitive reactions along a DOC and apparent NO oxidation inhibition in the presence of hydrocarbons [151]. 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 [142, 149]. 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 [142-143, 147-149, 151, 162, 164].

In this chapter, 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.

5.2 Experimental

5.2.1 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 [183]. 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.

5.2.2 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.

5.2.3 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 5.1. 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.

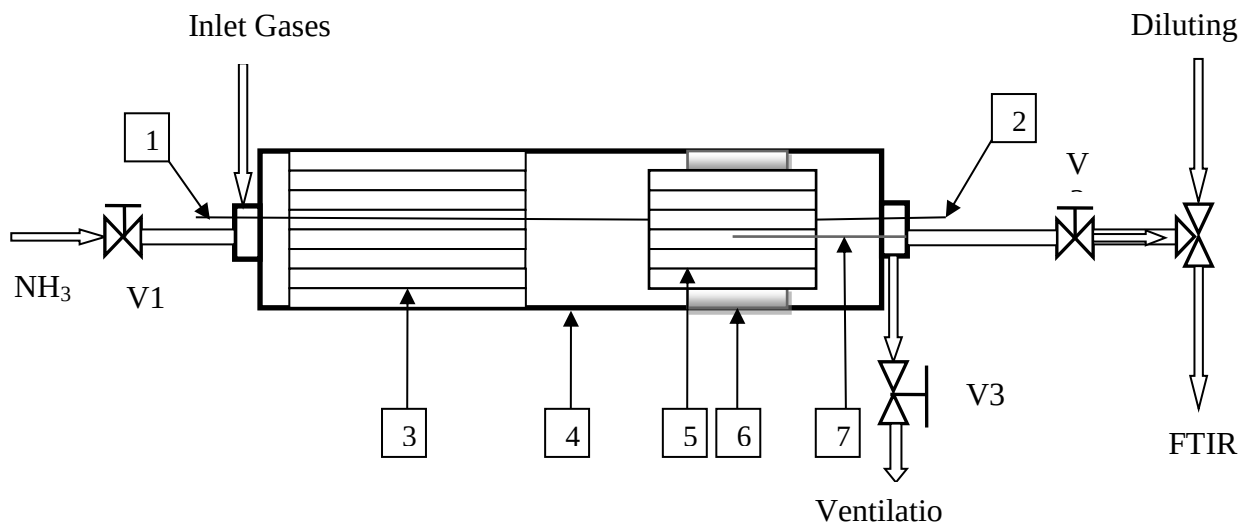


Figure 5.1 SCR reactor and spatial resolution sampling unit: (1) inlet thermocouple, (2) outlet thermocouple, (3) hollow quartz tubes, (4) quartz reactor tube, (5) catalyst monolith, (6) insulation/wrapping material, (7) silica capillary.

All the gases were supplied by Airgas, except N_2 , 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 NO_2 and NH_3 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 ($NO+NO_2$), 400 ppm NH_3 , 10% O_2 , 5% H_2O , 7% CO_2 and balance N_2 , and the total gas flow rate was 4.8 L/min, corresponding to a gas hourly space velocity (GHSV) of $48,000\text{ h}^{-1}$. For NH_3 oxidation tests, the NH_3 inlet concentration was 360 ppm, while O_2 , H_2O and CO_2 were the same as above, and the GHSV was $48,000\text{ h}^{-1}$. For NO oxidation, the NO inlet concentration was 200 ppm, while O_2 , H_2O and CO_2 levels were the same as above, and the GHSV was $30,000\text{ h}^{-1}$. For NH_3 adsorption, the NH_3 inlet concentration was 200 ppm, while O_2 , H_2O and CO_2 were the same as above, and the GHSV was $30,000\text{ h}^{-1}$. The quantity of adsorbed NH_3 was measured through NO titration after the catalyst was saturated.

5.3 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.

5.3.1 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 NH₃, and NH₃ 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 5.2(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 NH₃ conversions observed during standard SCR, fast SCR, and NH₃ 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 5.2(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.

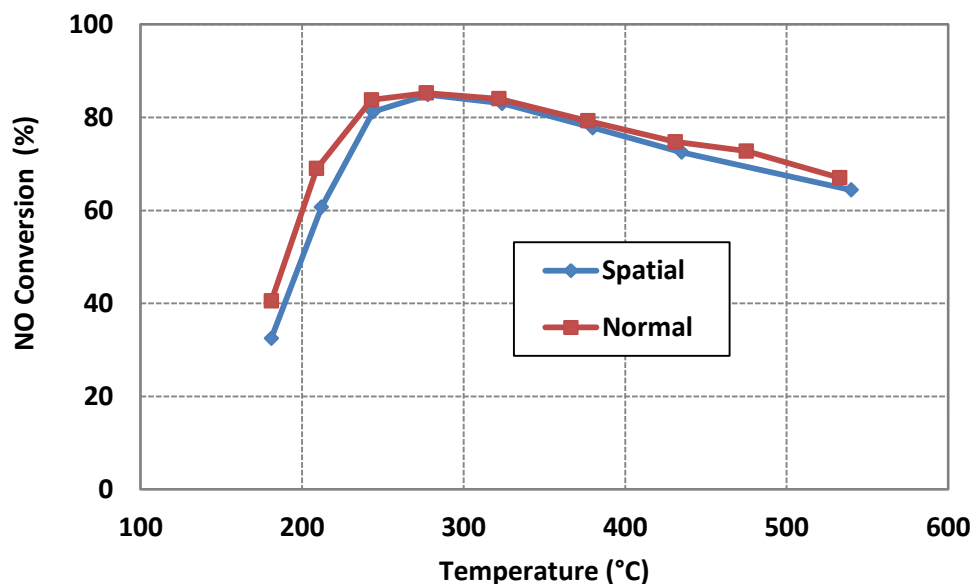


Figure 5.2(a) Standard SCR NO conversion comparison between normal and spatially-resolved tests for the medially aged catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

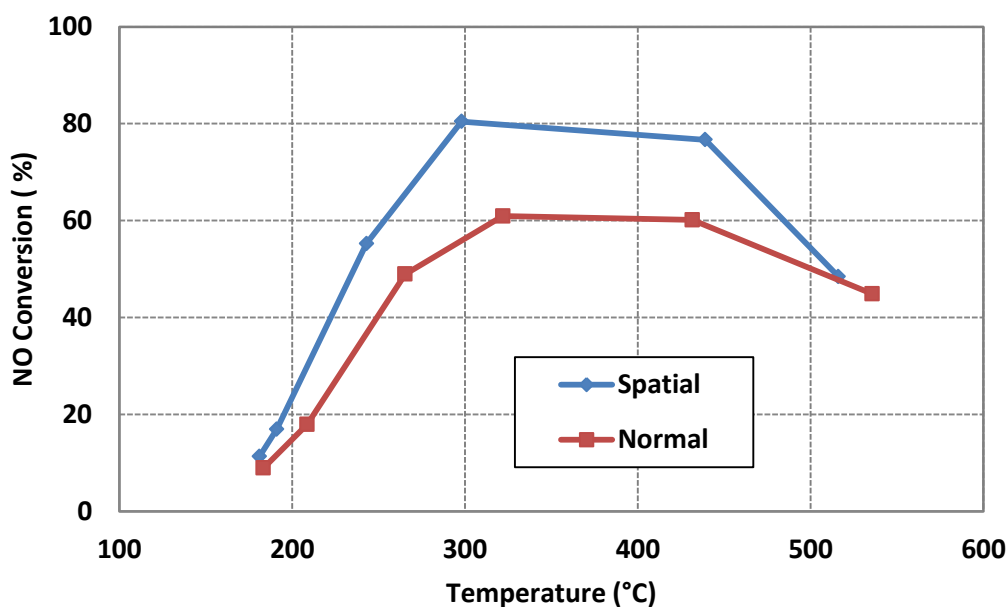


Figure 5.2(b) Standard SCR NO conversion comparison between normal and spatially-resolved tests for the highly aged catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

Based on the above results, the homogeneity of catalyst aging was evaluated for the three aged catalyst samples. Standard SCR, fast SCR and NH₃ 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 5.3 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).

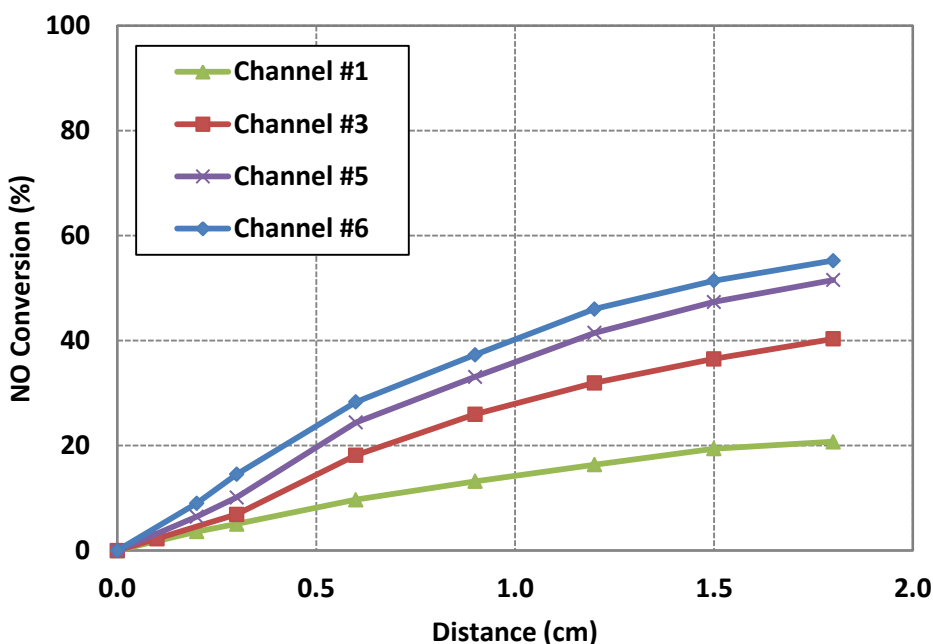


Figure 5.3(a) Standard SCR NO conversions at 250°C in channels located at different radial positions in the highly aged catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

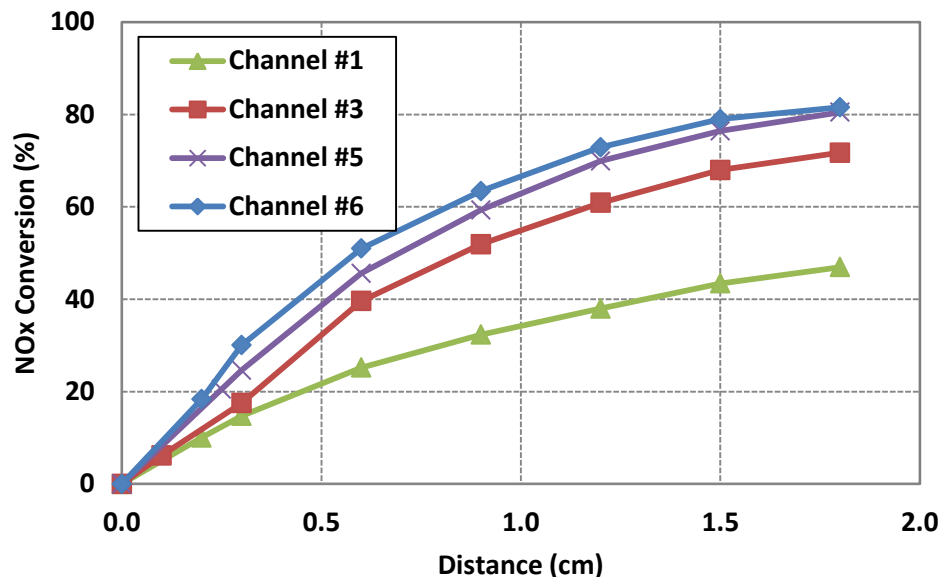


Figure 5.3(b) Fast SCR NO_x conversions at 250°C in channels located at different radial positions in the highly aged catalyst. GHSV = 48, 000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 200 ppm, NO₂ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

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 [113, 177], 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 5.2(b). The reason for the small difference at low temperature is that NO oxidation is the controlling step for standard SCR at low temperatures [70, 75]. 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 NH₃. As NH₃ 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.

5.3.2 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 5.4. 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 [184] over copper compounds. NO₂ 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 [113]. 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.

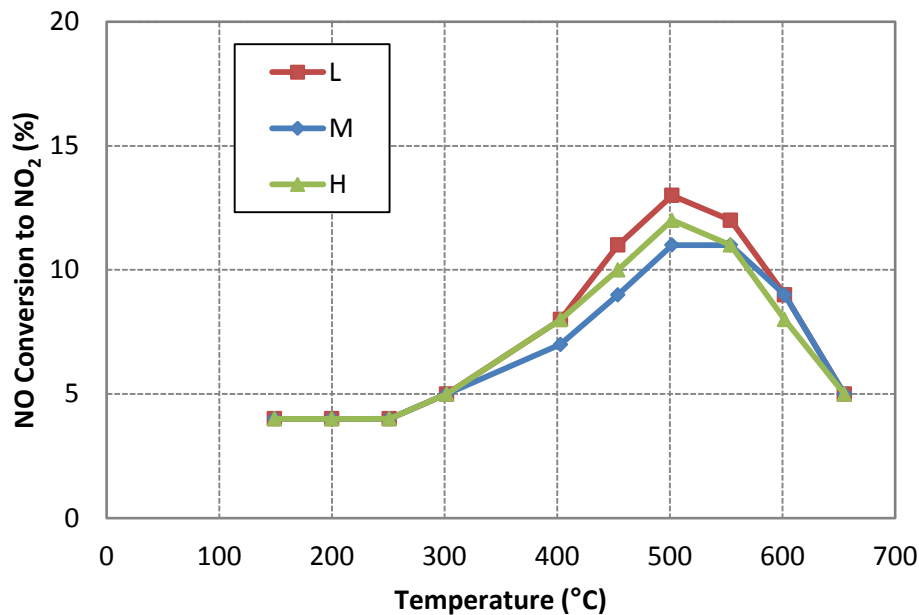


Figure 5.4 Effect of aging on NO oxidation by O_2 to NO_2 as a function of temperature during a normal test. GHSV = $30,000\text{ h}^{-1}$, inlet concentrations NO = 200 ppm, O_2 = 10%, H_2O = 5%, CO_2 = 7%.

5.3.3 Spatially-resolved standard SCR reaction

5.3.3.1 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 5.5 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 5.5(a), the NH_3 conversion increased monotonically with temperature and catalyst length. Figure 5.5(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.

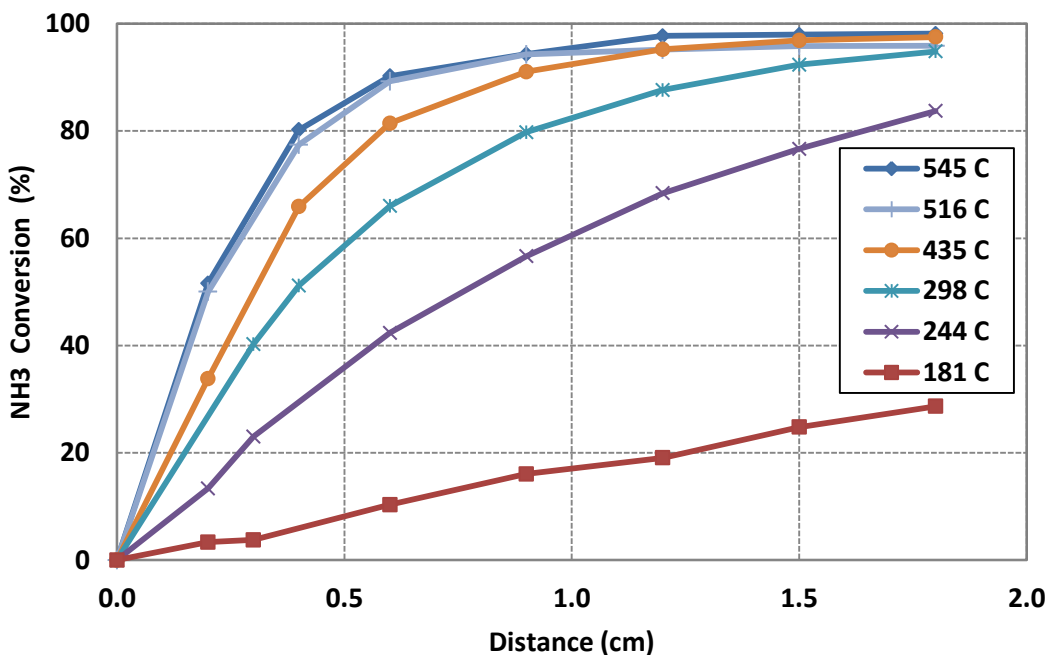


Figure 5.5(a) NH₃ conversion as a function of catalyst length and temperature when testing the lightly aged catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

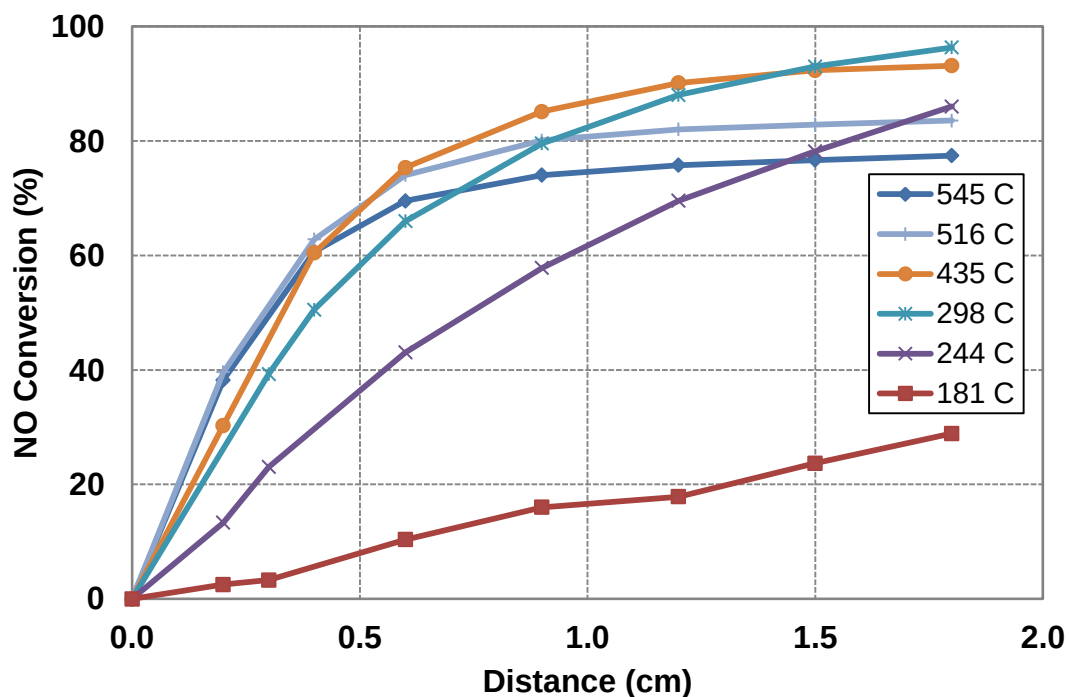


Figure 5.5(b) NO conversion as a function of catalyst length and temperature when testing the lightly aged catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

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 5.6. 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.

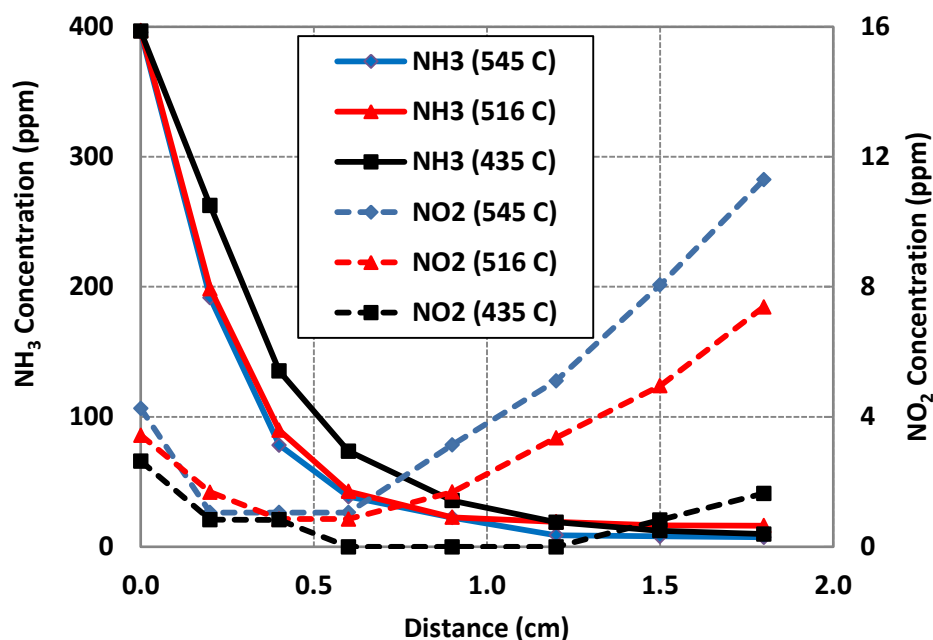


Figure 5.6 NH_3 and NO_2 concentration profiles along the lightly aged catalyst. GHSV = $48,000 \text{ h}^{-1}$, inlet concentrations $\text{NH}_3 = 400 \text{ ppm}$, $\text{NO} = 400 \text{ ppm}$, $\text{O}_2 = 10\%$, $\text{H}_2\text{O} = 5\%$, $\text{CO}_2 = 7\%$.

5.3.3.2 Hydrothermal aging effects on NO and NH_3 conversion for the standard SCR reaction

The effects of catalyst hydrothermal aging on NO and NH_3 conversion in standard SCR were investigated using both normal and spatially-resolved test procedures. Results obtained at 1.8 cm from the inlet of the catalyst during spatially-resolved experiments are shown in Figure 5.7, where NO and NH_3 conversions are plotted as a function of reaction temperature. Although normal test data could be used in such a plot, the data presented previously demonstrated radial gradients for the highly aged sample. Thus the spatially-resolved test results provide a more direct comparison for the hydrothermal aging temperature effect (with the central channel being measured at 800°C during the aging). The maximum NO

conversion for all three catalysts was attained at around 300°C, while NH₃ conversion increased with temperature monotonically. Differences in conversion trends between NO and NH₃ started after 300°C, where NH₃ oxidation by oxygen became significant. The NO conversion differences between the medially and lightly aged catalysts were smaller than the differences between medially and highly aged catalysts, even though the hydrothermal aging temperature difference between the latter pair was smaller than the former, indicating that the change in performance, and in this case catalyst structure, is not linear with hydrothermal aging temperature. This again demonstrates that, for 72 hours hydrothermal aging, the critical temperature for the dramatic damage to the catalyst structure lies between 700 and 800°C.

From the spatially-resolved test data shown in Figure 5.7, NH₃ overconsumption became significant at temperatures higher than 300°C and its significance increased with reaction temperature. The effect of catalyst hydrothermal aging on NH₃ oxidation with oxygen, or reaction selectivity, will be specifically discussed in the next section. These data also show that for the standard SCR reaction, NH₃ overconsumption over the highly aged catalyst increased more than those for the medially and lightly aged catalysts at high temperatures.

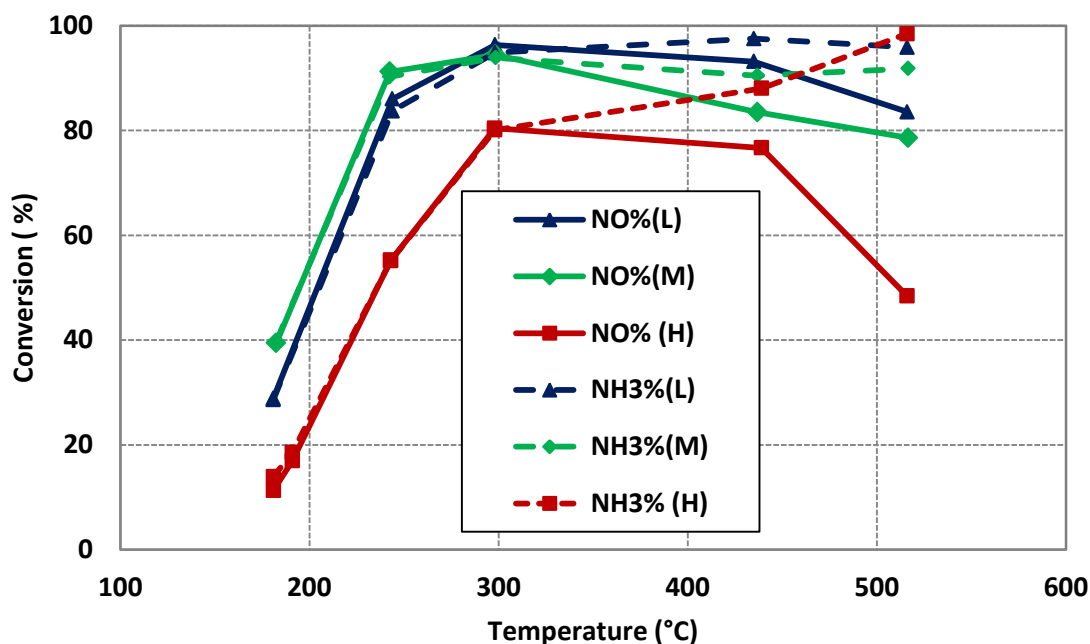


Figure 5.7 Catalyst hydrothermal aging effect on NO and NH₃ conversions for standard SCR as a function of temperature; spatially-resolved test method with these data obtained at the 1.8 cm position. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

Hydrothermal aging also impacts NH₃ adsorption, which of course influences reactivity [185]. Adsorption experimental data, shown in Figure 5.8, demonstrate that hydrothermal aging, especially high temperature aging, can significantly reduce Cu-zeolite catalyst adsorption capacity for NH₃. In addition,

as discussed previously, NO oxidation is minimally affected by hydrothermal aging. With these two points, the performance difference between the highly aged and medially and/or lightly aged catalysts can be explained. At temperatures below 300 °C, NO oxidation to NO₂ is the controlling step in standard SCR [70, 75]. While the NO oxidation ability is approximately the same for all three catalysts, at low temperatures the difference in NH₃ adsorption is significantly different and likely the main cause for the overall NO conversion difference between highly aged and medially and/or lightly aged catalysts. As the reaction temperature increases, the overconsumption of NH₃ by oxygen over the highly aged catalyst is the main cause for the NO conversion differences observed, as discussed in the next section.

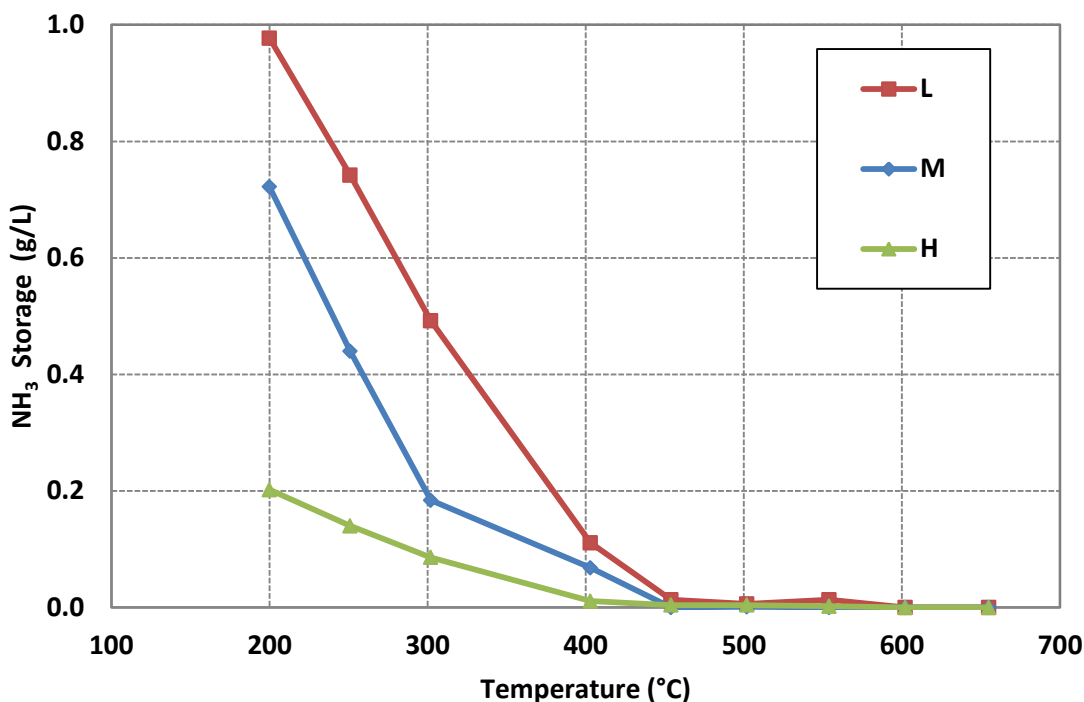


Figure 5.8 Catalyst hydrothermal aging effect on NH₃ storage as a function of temperature. GHSV = 30,000 h⁻¹, inlet concentrations NH₃ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.3.3.3 Hydrothermal aging effect on NH₃ overconsumption

In standard SCR, it has been reported by researchers that at higher temperature, the oxidation of NH₃ by oxygen is detrimental to the performance of the catalyst [186]. In order to determine the significance of hydrothermal aging on NH₃ overconsumption, the effect of catalyst aging on the selectivity of NH₃ oxidation by O₂ over NH₃ oxidation by NO was investigated. To calculate the value of this selectivity, it was assumed that when NO is reduced by NH₃ under standard SCR conditions, the reaction proceeds with NO and NH₃ consumed in an equimolar amount,



Therefore, the quantity of NO consumed is the quantity of NH₃ oxidized by NO, and the difference between total NH₃ consumption and NO consumption is the quantity of NH₃ overconsumption, which under steady-state conditions represents NH₃ oxidation by oxygen. With the spatial resolution technique, the quantities of NH₃ and NO consumed for each section were calculated. The selectivity of NH₃ oxidation by O₂ over NH₃ oxidation by NO in each section was calculated as follows:

$$S = (\text{NH}_3 \text{ consumed} - \text{NO consumed}) / \text{NO consumed} \quad (5.2)$$

The selectivity data are plotted in Figure 5.9. As shown in Figure 5.7, NH₃ overconsumption was not evident at temperatures below 300°C. At temperatures above 435°C, the significance of NH₃ overconsumption increased with reaction temperature, thus only high temperature data are shown in Figure 5.9. There is little difference in selectivity between the lightly and medially aged catalysts. At around 516°C, NH₃ oxidation by O₂ over the highly aged catalyst was more significant than over medially and lightly aged catalysts. Delahay et al [187] found that large CuO particles are more active than cationic and/or oxocationic Cu species in Cu-FAU for NH₃ oxidation by oxygen. The results reported here suggest that there are CuO particles present in the highly aged Cu-zeolite catalyst.

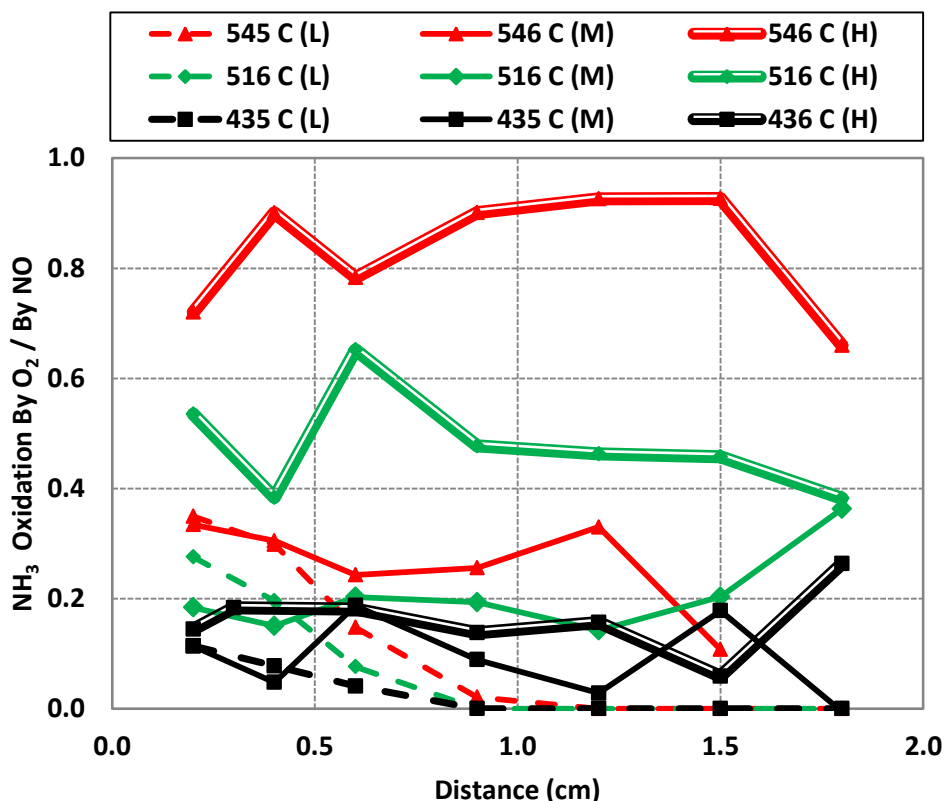


Figure 5.9 Effects of temperature and catalyst hydrothermal aging on the selectivity of NH₃ oxidation by O₂ over NH₃ oxidation by NO. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.3.4 Spatially-resolved fast SCR reaction

5.3.4.1 Temperature effect on concentration/conversion profiles

Similar to the experiments performed for the standard SCR reaction, the effect of temperature on concentrations for the fast SCR reaction along catalyst length was studied. NO conversion profiles as a function of catalyst length and temperature for the highly aged catalyst under fast SCR conditions are shown in Figure 5.10. The highest NO conversion was attained around 300°C. Interestingly, at the front of the catalyst, for the 516°C reaction temperature, the NO conversion was negative, which indicates that part of NO₂ in the system was decomposed into NO, driven by thermodynamic equilibrium constraints at high temperature. And as will be shown later, NO₂ in an equimolar NO/NO₂ mixture can decompose over the Cu-zeolite catalyst to a significant extent at temperatures above 500°C, negatively affecting the fast SCR system, which will be discussed in the following sections. Similar to that observed for the standard SCR reaction, the NH₃ conversion for all three aged catalysts (data not shown) increased monotonically with temperature while NO_x conversion dropped at high temperatures, demonstrating that NH₃ overconsumption occurs during the fast SCR reaction as well.

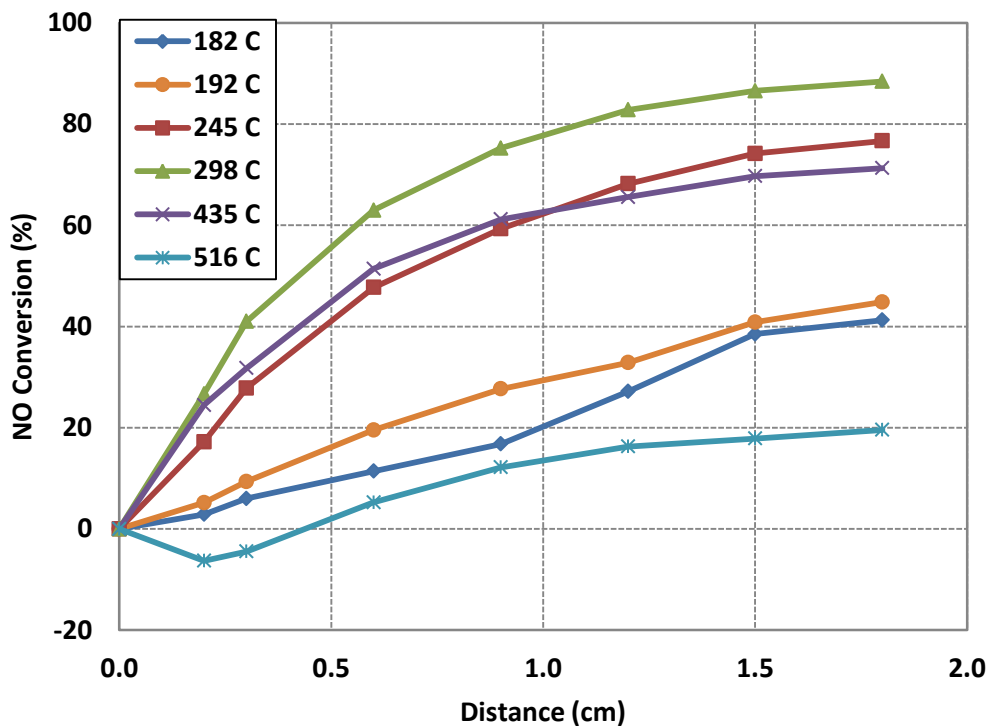


Figure 5.10 Fast SCR NO conversion profiles as a function of temperature and catalyst length over the highly aged Cu-zeolite catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NO = 200 ppm, NO₂ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.3.4.2 Effect of hydrothermal aging on NO_x and NH₃ conversion in fast SCR reaction

The effects of catalyst hydrothermal aging on NO_x and NH₃ conversion under fast SCR reaction conditions were investigated. The conversions at 1.8 cm from the catalyst inlet obtained during spatially resolved tests are shown in Figure 5.11. The highest overall NO_x conversion was again attained around 300°C for the three aged catalysts. NH₃ overconsumption again became significant at temperatures higher than 300°C. In comparing these data to those obtained under the standard SCR reaction conditions, differences are evident. First, NH₃ overconsumption over the highly aged catalyst at high temperatures under fast SCR reaction conditions was not as serious as that in the standard SCR reaction system, likely due to NH₃ oxidation via O₂ being less competitive with fast SCR compared to standard SCR. Aggravating this, the reduced capability of the catalyst in converting NO and/or NO_x into N₂ after degradation, allows more extensive NH₃ overconsumption under the standard SCR conditions. For the lightly and medially aged catalysts, no significant differences were observed. The overconsumption extent was also lower for these two samples.

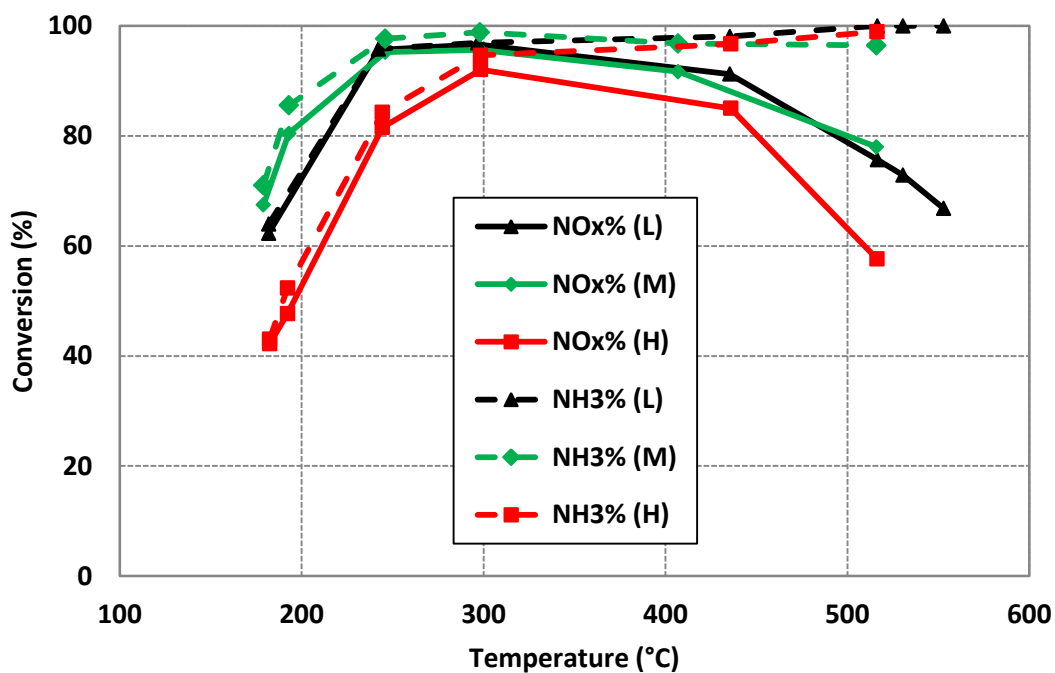


Figure 5.11 Effect of hydrothermal aging on NO_x and NH₃ conversions as a function of temperature under fast SCR conditions. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 200 ppm, NO₂ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

Another difference between the standard and fast SCR results that was observed is the decreased impact of hydrothermal aging on the fast SCR reaction relative to the standard SCR reaction. For example, in the

case of the standard SCR reaction, NO conversions attained using the lightly aged catalyst, at 180 and 516°C, were almost twice that of the values attained when testing the highly aged catalyst at those temperatures. However, in the case of the fast SCR reaction, NO_x conversions over the lightly aged catalyst were at most 1.5 times the respective values attained from the highly aged catalyst. This suggests that the fast SCR reaction mechanism and the sites involved are less susceptible to thermal aging. Also however, at higher temperatures, another possibility that reduces the NO_x conversion difference between the highly and lightly aged catalysts for fast SCR, as will be discussed in the next section, is that NO₂ decomposition is less significant after hydrothermal aging.

5.3.4.3 Effect of hydrothermal aging on NO₂ decomposition during the fast SCR reaction

The effect of catalyst hydrothermal aging on NO₂ decomposition as a function of temperature was characterized to understand when the fast SCR reaction might be impacted by NO₂ loss. An equimolar NO/NO₂ mixture was introduced into the reactor together with 10% O₂, 5% H₂O and 7% CO₂, and the NO₂ concentration change along the catalyst length was monitored at 490 and 540°C in three different channels, one at the edge (channel No. 1), one close to the center (channel No. 5), and the third one in between (channel No. 3) over the highly aged Cu-zeolite catalyst. The results are shown in Figure 5.12. As expected, the extent of NO₂ decomposition increased with temperature. Based on the evidence discussed previously regarding the heterogeneity in deactivation resulting from the temperature difference along the radial direction during the 800°C hydrothermal deactivation process, the hydrothermal aging extent in channel No. 1 was the most significant of the three channels and that for channel No. 5 was the least. From the data shown in Figure 5.11, it is also apparent that the Cu zeolite catalyst's ability in promoting NO₂ decomposition decreases with increasing hydrothermal aging. This combination of changes explains why there is less effect on the fast SCR reaction than that on the standard SCR reaction, as was discussed previously. The detrimental hydrothermal aging effect is partially reduced with decreasing NO₂ decomposition extents. This decreased NO₂ decomposition extent allows the NH₃ SCR reaction to compete against NH₃ overconsumption at high temperatures.

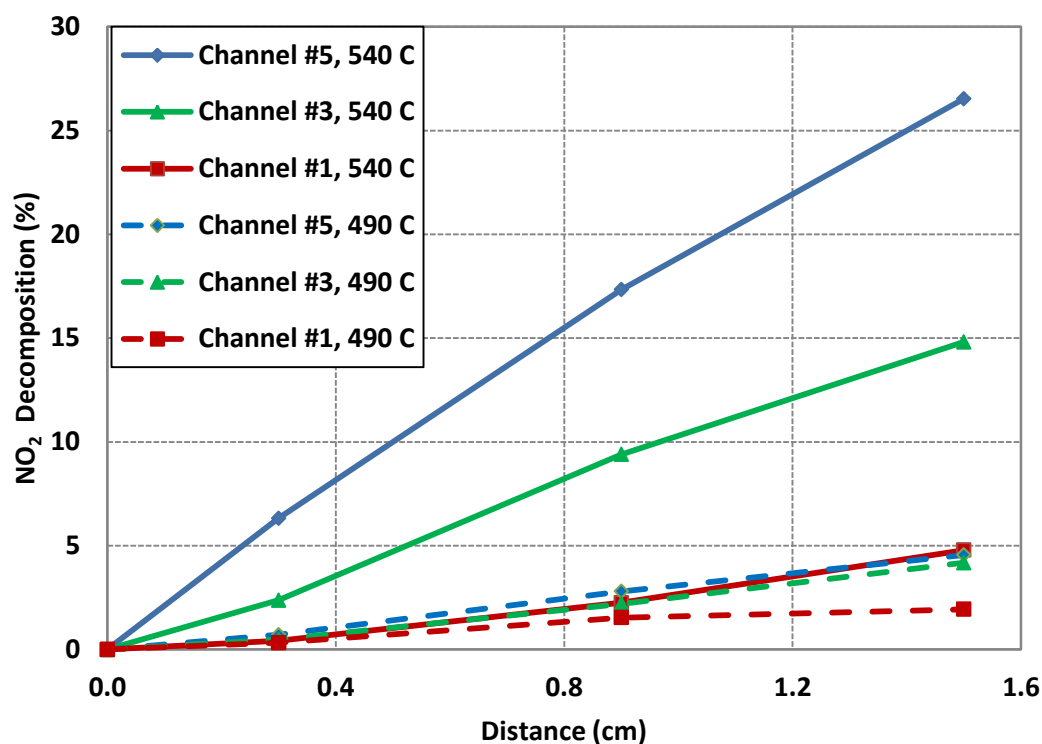


Figure 5.12 NO₂ decomposition as a function of temperature and catalyst length in different channels over the highly aged Cu-zeolite catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NO = 200 ppm, NO₂ = 200 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.3.5 Spatially-resolved NH₃ oxidation

5.3.5.1 Temperature effect on concentration/conversion profiles

As discussed, the consumption of NH₃ by oxygen instead of being used in the SCR reactions is a critical negative impact on the overall performance. NH₃ oxidation conversions are shown in Figure 5.13. NH₃ oxidation occurred at all temperatures tested. For temperatures below 400°C, NH₃ oxidation conversion increased almost linearly along the catalyst length. At temperatures higher than 500°C, NH₃ was consumed by oxygen very quickly, suggesting that NH₃ overconsumption will be a very strong competitor with NH₃ SCR at high temperatures. Also, as shown in the figure, at 615°C nearly 40 ppm NO_x was produced by the catalyst outlet.

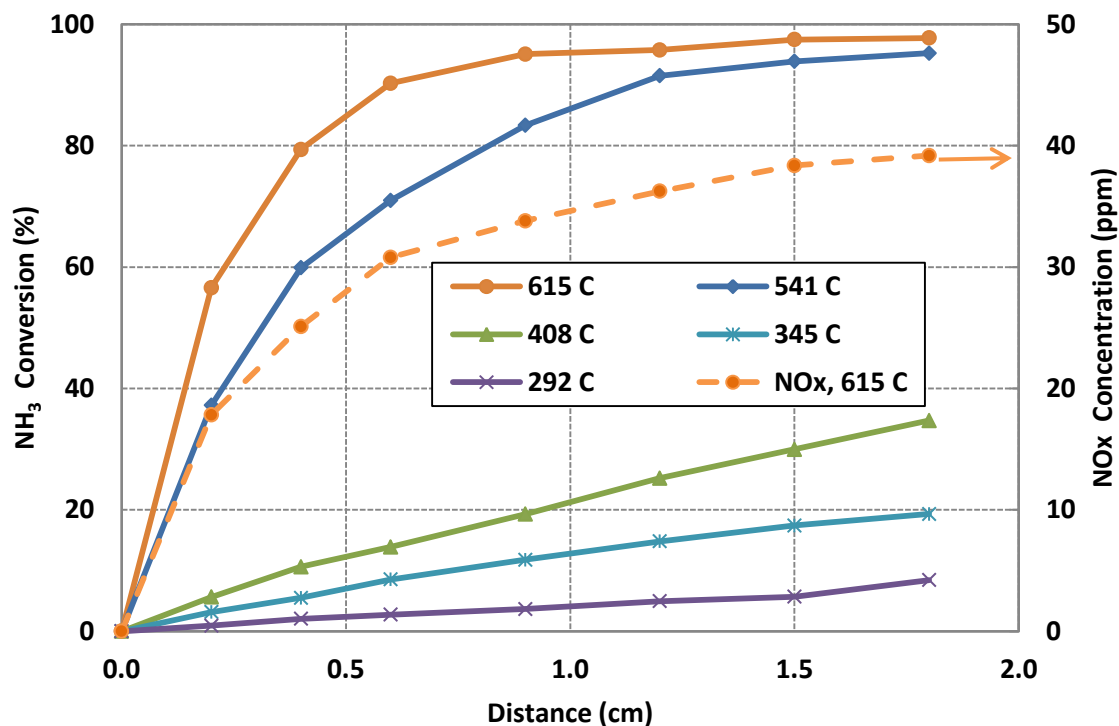


Figure 5.13 NH₃ oxidation conversion profiles as a function of catalyst length and temperature for the lightly aged Cu-zeolite catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 360 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.3.5.2 Hydrothermal aging impact on NO_x generation from NH₃ oxidation

The effect of catalyst hydrothermal aging on NO_x output during NH₃ oxidation as a function of temperature was investigated and the data are shown in Figure 5.14. These data do not suggest that when no NO_x is evident, none was produced via NH₃ oxidation, just that any that was produced was subsequently consumed via residual NH₃. Measureable NO and NO₂ amounts were observed at temperatures higher than 540°C. In comparing the extent of degradation, the highly aged Cu-zeolite catalyst resulted in the highest concentration of NO_x, while the medially aged catalyst produced the least.

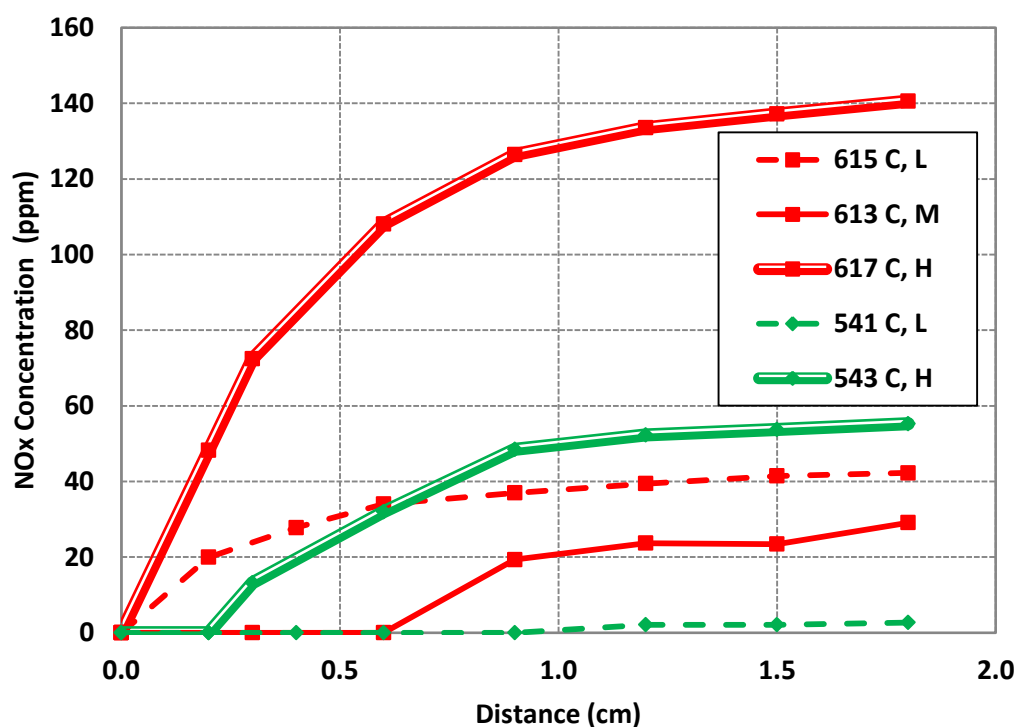


Figure 5.14 Hydrothermal aging impact on NO_x output during NH₃ oxidation as a function of temperature and catalyst position. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 360 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

The NH₃ conversions as a function of temperature and catalyst length during NH₃ oxidation are plotted in Figure 5.15. NH₃ conversion obviously depends on reaction temperature. The lightly aged catalyst resulted in the highest NH₃ conversion rates from 300 to 620°C. The data plotted in Figure 5.15(a) show that between 300 and 350 °C, NH₃ conversion rates decreased monotonically with hydrothermal aging extent. But at higher temperatures, Figure 5.15(b), higher NH₃ conversion rates were observed over the highly aged sample relative to the medially aged catalyst. As shown in Figure 5.14, the highly aged catalyst has greater capability in producing NO_x through NH₃ oxidation at high temperatures. When there is NO_x in the system, SCR can of course occur. The consumption of NH₃ can therefore include both oxidation and SCR. Therefore, the highly aged catalyst is more active than the medially aged catalyst for NH₃ conversion due to its higher capability in producing NO_x at high temperatures.

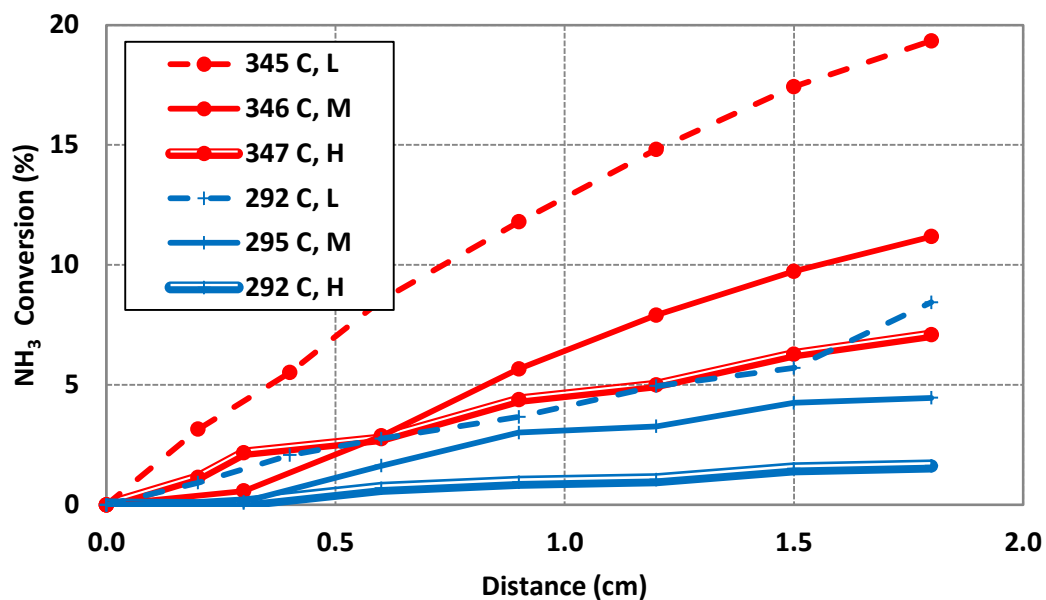


Figure 5.15(a) Catalyst hydrothermal aging effect on NH_3 conversion in NH_3 oxidation as a function of temperature (300 °C – 350 °C). GHSV = 48,000 h^{-1} , inlet concentrations NH_3 = 360 ppm, O_2 = 10%, H_2O = 5%, CO_2 = 7%.

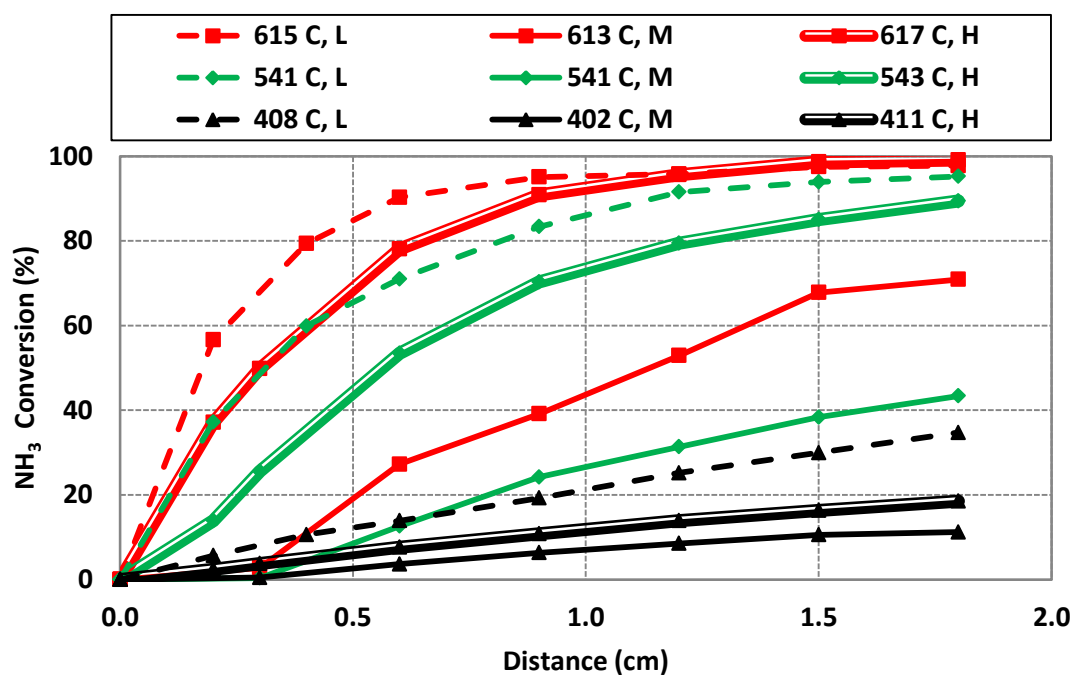


Figure 5.15(b) Catalyst hydrothermal aging effect on NH_3 conversion in NH_3 oxidation as a function of temperature (400°C – 620°C). GHSV = 48,000 h^{-1} , inlet concentrations NH_3 = 360 ppm, O_2 = 10%, H_2O = 5%, CO_2 = 7%.

5.3.6 Spatially-resolved effect of NO:NO₂ ratio

5.3.6.1 Effect of NO:NO₂ ratio on SCR

In order to understand the effect of NO to NO₂ ratio on NH₃ SCR performance, NO:NO₂ ratios were varied, from 400 ppm NO:0 ppm NO₂ to 0 ppm NO:400 ppm NO₂, at 200°C for the three differently aged Cu-zeolite catalysts. The NO_x conversion results as a function of NO:NO₂ and catalyst position for the medially aged catalyst are shown in Figure 5.16. The NO_x conversion was highest, reaching 80%, as expected, when the NO:NO₂ ratio was 1:1, since this matches the fast SCR equimolar feed conditions. In comparing the initial reaction rates at the 0.3 cm position in the catalyst, the fast SCR reaction rate is >2 times higher than the standard SCR reaction rate and more than 3 times the reaction rate for NO₂ SCR. The NO_x conversions for NO:NO₂ ratios around 2:1 and 3:5 are very close. The main reason for this similarity in conversion is that at 200°C, the fast SCR reaction is the dominant reaction, leading to 2/3 of the entering NO_x being consumed.

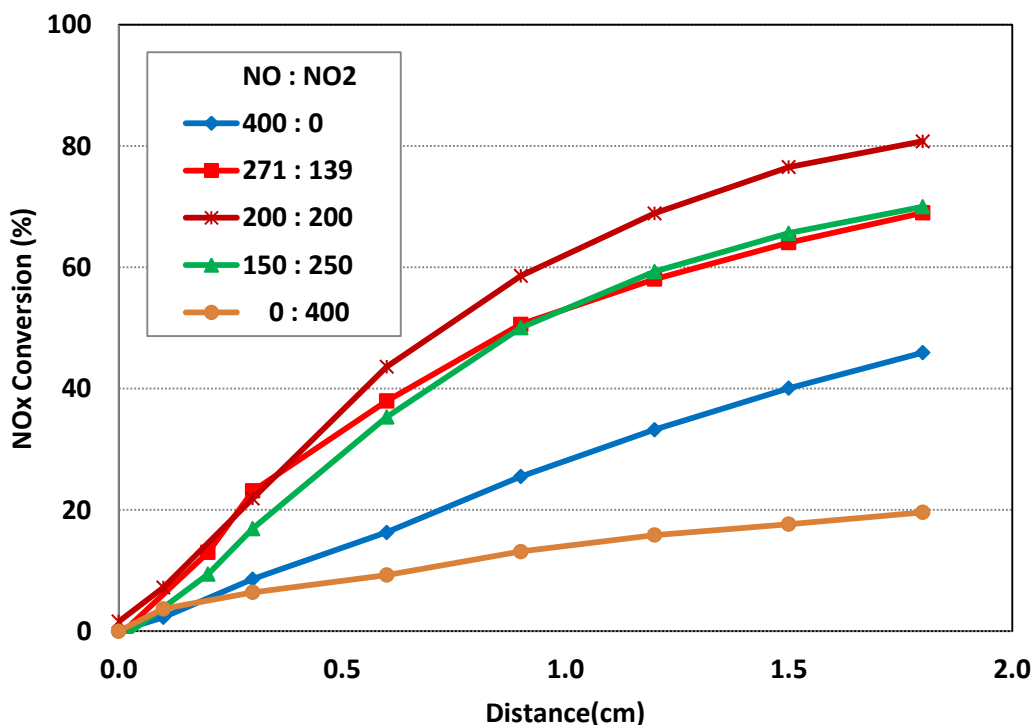


Figure 5.16 NO_x conversion profiles as a function of catalyst length and NO:NO₂ concentration over the medially aged Cu-zeolite catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO_x = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.3.6.2 Reaction sequence

When both NO and NO₂ are part of the inlet gases, in theory all three SCR reactions can occur. To determine which are occurring, the amounts of NO and NO₂ consumed along the catalyst length need to be measured and compared. The reduction in NO and NO₂ concentrations over unit lengths of catalyst for the lightly aged catalyst, when the inlet concentrations of NO and NO₂ were 200 ppm each, are shown in Figure 5.17. At 182°C, the consumption of NO₂ is slightly higher than that of NO through the catalyst, indicating that the main reaction is the fast SCR reaction while a small amount of reaction between NH₃ and NO₂ occurs simultaneously. At 297°C, the consumption of NO and NO₂ along the catalyst are the same, demonstrating that fast SCR is the only reaction occurring. At 516°C, more NO₂ was consumed in the front portion of sample, relative to NO, but towards the back portion, 1:1 consumption is observed indicating that only fast SCR occurs there. This initially larger NO₂ consumption is likely associated with NO₂ decomposition to NO, and NO₂ SCR.

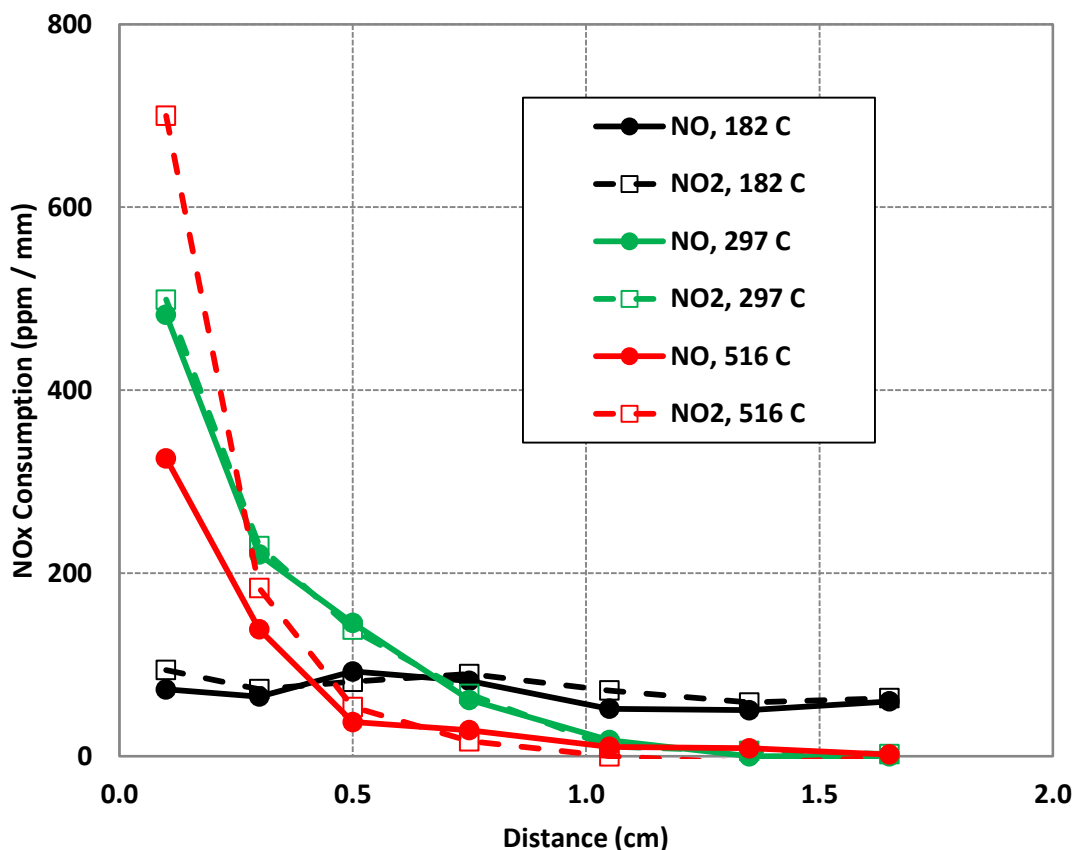


Figure 5.17 Change of NO and NO₂ consumption over unit lengths of catalyst along the lightly aged catalyst as a function of reaction temperature (inlet NOx concentration ratio NO:NO₂ = 200:200). GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NOx = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

The consumption of NO and NO₂ along the lightly aged catalyst at two different temperatures, with inlet NO and NO₂ concentrations of 262 and 126 ppm, respectively, are shown in Figure 5.18. At 193°C, in the first 0.5 cm section of the catalyst, the fast SCR reaction dominates and a small amount of reaction between NH₃ and NO₂ is observed. As the NO₂ concentration drops, the standard SCR reaction becomes more significant, although the fast SCR reaction obviously still occurs. At 553°C, within the first 0.3 cm section of the catalyst the main reaction is again the fast SCR reaction. Beyond the first 0.5 cm of the catalyst, the standard SCR reaction is the main reaction due to the lack of NO₂.

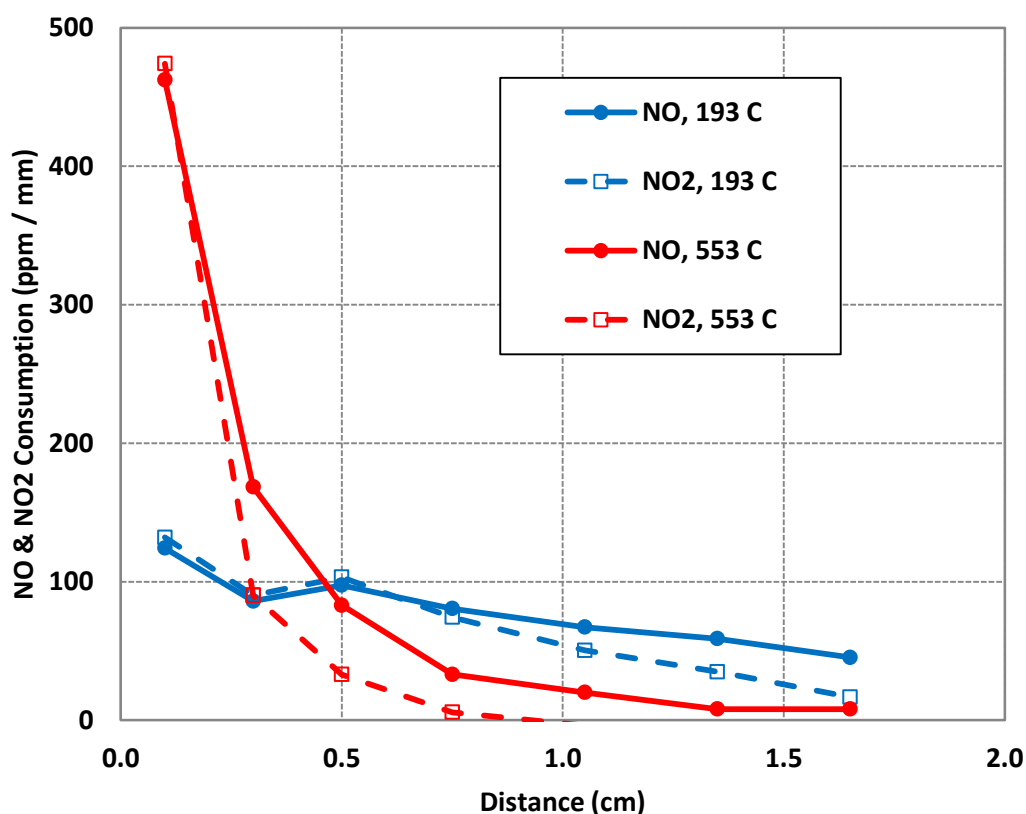


Figure 5.18 Change in NO and NO₂ consumption per unit length of catalyst along the lightly aged catalyst as a function of reaction temperature (inlet NO_x concentration ratio NO:NO₂ = 262:126). GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO_x = 388 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.3.6.3 Effect of hydrothermal aging on NO_x reduction with varying NO:NO₂ ratio

The effects of hydrothermal aging on fast SCR and standard SCR were discussed above. In this section, the other three NO:NO₂ ratios evaluated, 150:250, 271:139 and 0:400, are included. As shown in Figure 5.19, in general, hydrothermal aging reduced the SCR reaction rates regardless the NO:NO₂ ratio. The effect of hydrothermal aging on NO and NO₂ conversions at 200°C are shown in Figure 5.20, and the NO

and NO_2 conversions decreased almost in parallel, suggesting that the aging effects on the SCR reactions with various $\text{NO}:\text{NO}_2$ ratios are not differentiated at 200°C .

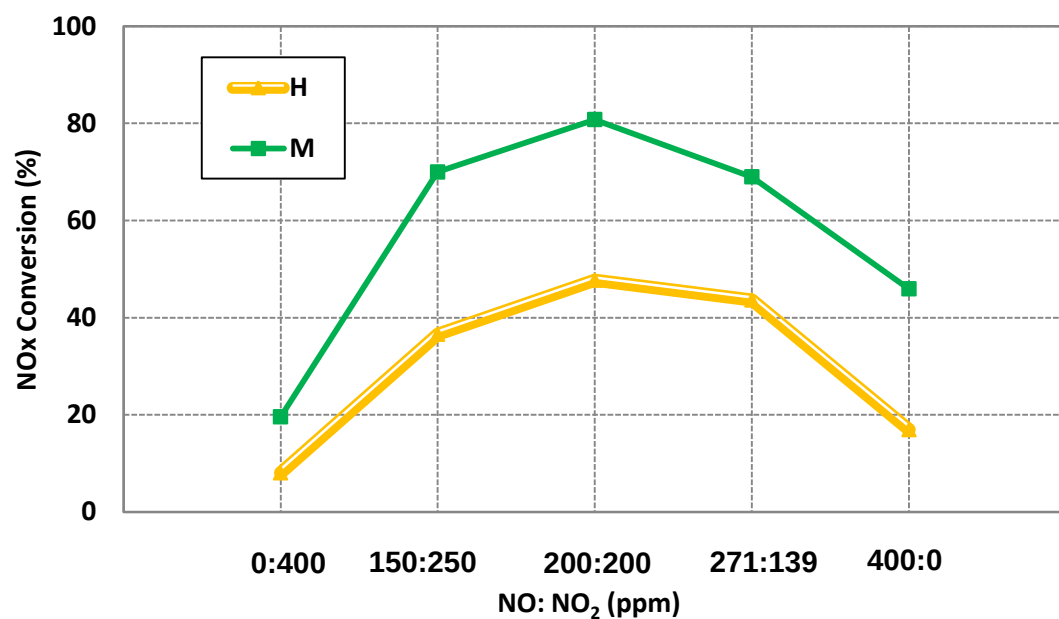


Figure 5.19 Catalyst hydrothermal aging effect on NO_x conversion for various NO: NO₂ ratios (200°C). GHSV = $48,000 \text{ h}^{-1}$, inlet concentrations $\text{NH}_3 = 400 \text{ ppm}$, $\text{NO}_x \sim 400 \text{ ppm}$, $\text{O}_2 = 10\%$, $\text{H}_2\text{O} = 5\%$, $\text{CO}_2 = 7\%$.

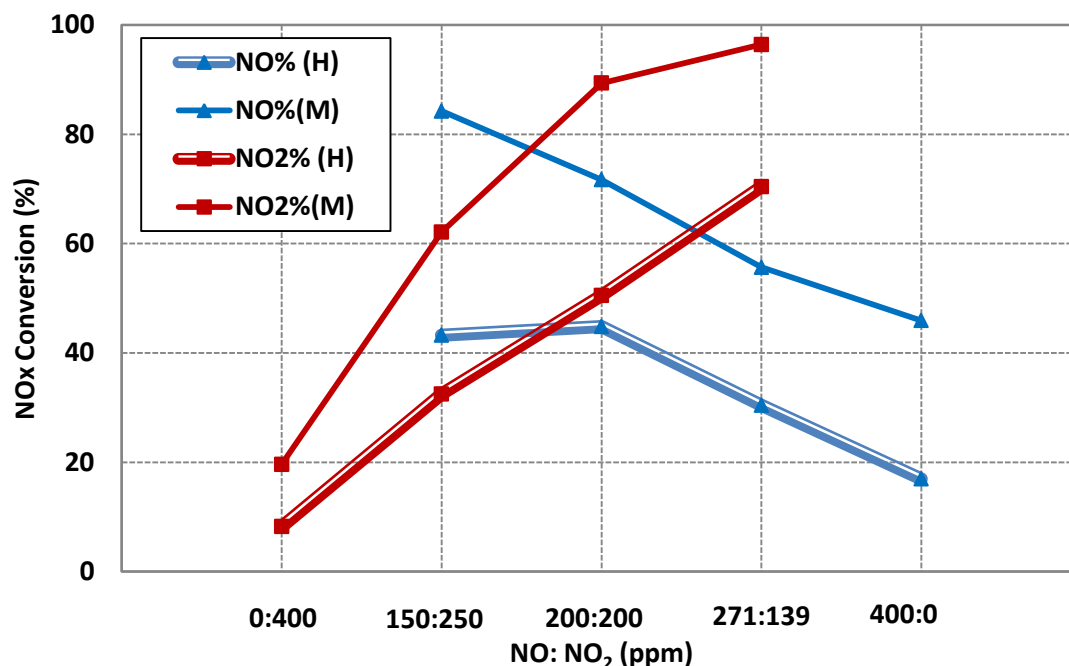


Figure 5.20 Hydrothermal aging effect on NO and NO₂ conversions for various NO:NO₂ ratios (200°C). GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO_x ~ 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

5.4 Conclusions

Comparison between spatially-resolved test results and normal test results demonstrated that spatial resolution with FTIR is a reliable test technique. For the Cu-zeolite catalyst, our experiments suggest that the critical temperature at which the zeolite structure used experiences dramatic change lies between 700 and 800°C. For these tests, during hydrothermal aging in the tube reactor at 800°C, due to a radial temperature distribution in the reactor, heterogeneity in aging occurred and hence resulted in activity distribution along the radial direction, but only for the highly aged sample.

Hydrothermal aging had little effect on NO oxidation activity. For standard SCR and fast SCR, NH₃ conversions changed monotonically with temperature and catalyst length. NH₃ overconsumption became significant when the reaction temperature was higher than 300°C, which limited the conversion of NO due to the lack of NH₃. Therefore, for standard SCR and fast SCR, NO_x conversion attained its maximum at 300°C. In fast and standard SCR, hydrothermal aging decreased reaction rates for SCR and NH₃ overconsumption simultaneously. Selectivity to NH₃ overconsumption was higher over the highly aged catalyst at high temperatures, >500°C. NO oxidation was observed 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 was more heavily

affected by hydrothermal aging than NO_x conversion for fast SCR. Correspondingly, NH₃ overconsumption was more significant under standard SCR conditions than that for fast SCR.

Along a monolithic catalyst channel, the extent of reaction changes with the NO:NO₂ composition. When there are both NO and NO₂ present in the inlet gas, the fast SCR reaction dominated, although NO₂ SCR was also observed at low temperatures. When NO₂ was consumed along the catalyst, standard SCR became significant. However, fast SCR at high temperatures was 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 helped maintain fast SCR reaction conditions in the catalyst. The effect of hydrothermal aging on NH₃ oxidation was more complicated. Generally, aging reduced NH₃ oxidation activity, but it did not change monotonically with aging extent; neither did the output of NO_x produced during NH₃ oxidation. However, the highly aged catalyst produced a higher proportion of NO_x. At 200°C, hydrothermal aging did not show appreciable effects on the SCR extent with various NO:NO₂ ratios.

This bulk of this chapter was published in 2012, Catalysis Today, Volume 197, 2012, pp. 9-17. Chapter numbers have been inserted to help the reader, and Figure numbers changed to reflect the chapter number.

Chapter 6 NH₃ Pulsing Adsorption and SCR Reactions over a Cu-CHA SCR Catalyst

6.1 Introduction

Nitrogen oxides (NO_x) are a significant source of air pollution, which can form ground level ozone and contribute to acid rain formation. Besides stationary sources, such as power plants and nitric acid factories, mobile sources are significant contributors to NO_x emissions. NO_x after-treatment systems for mobile sources differ depending on the engine. For gasoline engines, three-way catalysts (TWCs) have been very effective for the removal of NO_x from automotive exhaust [188], where expensive platinum group metals (PGM) are the active components, over which NO_x is reduced by CO or hydrocarbons. For diesel engines, lean NO_x traps (LNT) and selective catalytic reduction (SCR) catalysts are two approaches in eliminating NO_x. This paper focuses on SCR, where NO_x is reduced on a catalyst with NH₃ as the reductant.

Early studies showed that when NO_x is reduced over TWCs and LNT catalysts, NH₃ could form as a byproduct [23-28, 138]. Based on such findings, the concept of passive NH₃ SCR was recently proposed [139], as described by Figure 6.1. In this system, NH₃ is produced during rich operation, via reduction of the NO_x over the TWC, or LNT. The produced NH₃ is then stored on the downstream SCR catalyst, and can be used as the reductant to reduce NO_x during subsequent lean operation. So, for passive SCR systems, instead of supplying NH₃ via for example urea addition into the exhaust stream for the SCR reaction, NH₃ is produced on an upstream catalyst, and is then adsorbed on the SCR catalyst and used to reduce NO_x to N₂. However, where the NH₃ adsorbs, i.e. adsorption profiles along the length, whether it stays adsorbed, and where the subsequent reactions occur over SCR catalysts with pre-absorbed NH₃ are unknown. Considering that during its lifetime the SCR catalyst will experience high temperature excursions, the effects of thermal aging on the above are also of interest.

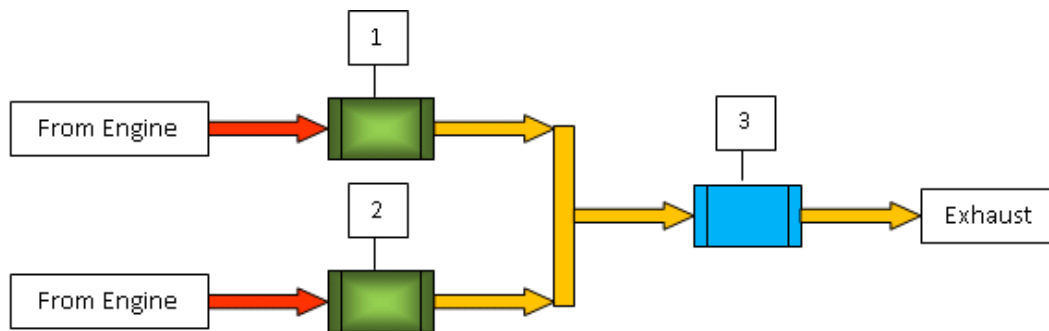


Figure 6.1 Passive SCR system illustration; (1) & (2) close-coupled three-way catalysts; (3) under-floor Cu-SCR catalyst

Spatially resolving reactions is becoming more common as a catalyst testing method in automotive applications; as such methods provide more information than integral (inlet and outlet), steady-state measurements and are therefore quite useful in developing and validating models [142-143]. Spatially Resolved Capillary Inlet Mass Spectrometry (SpaciMS) has been used to measure gas-phase concentrations along LNT catalysts, to investigate activity changes with exposure to sulfur for example [145-146]. These studies have shown different activity regions inside the catalyst and how they change as a function of sulfur poisoning. SpaciMS has also been used to monitor competitive reactions along a Diesel Oxidation Catalyst (DOC) and apparent NO oxidation inhibition in the presence of hydrocarbons [143, 146-147]. 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 [142, 149]. Such spatially resolved reaction 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 catalyst length, volume and distribution of active species. 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 [142-143, 146-148, 151, 162]. Spatially resolving gas concentrations with Fourier-Transform Infra-Red (FTIR) (SpaciFTIR) spectroscopy, however, has also been developed to investigate the performance and hydrothermal durability of zeolite based SCR catalysts [189-190]. Together with NO, NO₂, H₂O and CO₂, NH₃ concentrations along the length of SCR catalysts could be measured, avoiding 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.

In this chapter, SpaciFTIR was used to evaluate NH₃ adsorption profiles and how they are affected by temperature, time and concentration, how these profiles affect SCR reactions, and the effect of thermal aging on these.

6.2 Experimental methods

6.2.1 Catalyst

The catalyst used was supplied by BASF Corporation. The catalyst is a 100% ion exchanged Cu chabazite containing 2.8 wt.% copper expressed as Cu metal with a nominal silica to alumina ratio (molar) of 35:1. The exchanged zeolite was coated on 300 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 [183]. The sample used for these tests was cut from a full-size monolith and was 2.0 cm long and 1.6 cm in diameter. Compared with other zeolite-based catalysts, Cu chabazite has higher SCR

activity at low temperature, higher selectivity to N_2 , in particular low N_2O formation, better thermal durability and is relatively resistant to hydrocarbon inhibition. [191] Cu chabazite SCR catalysts are now considered the industry standard.

6.2.2 Hydrothermal aging

The catalyst was hydrothermally aged sequentially in two stages. After the first stage aging, the sample is labeled as lightly aged (16h at 500°C), and after the second stage as highly aged (72h at 700°C). The aging was in a horizontal quartz tube reactor, heated by an Applied Test Systems, Inc. Series 3210 temperature-controlled electric furnace. 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, corresponding to a gas hourly space velocity (GHSV) of 60,000 h^{-1} . The gas composition consisted of air and 10% H_2O .

6.2.3 Reactor set-up

The hydrothermally aged catalyst sample was wrapped with heat-expanding insulation material and inserted into another 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 6.2, where V1 to V4 are control valves to direct the flow of gases. 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.

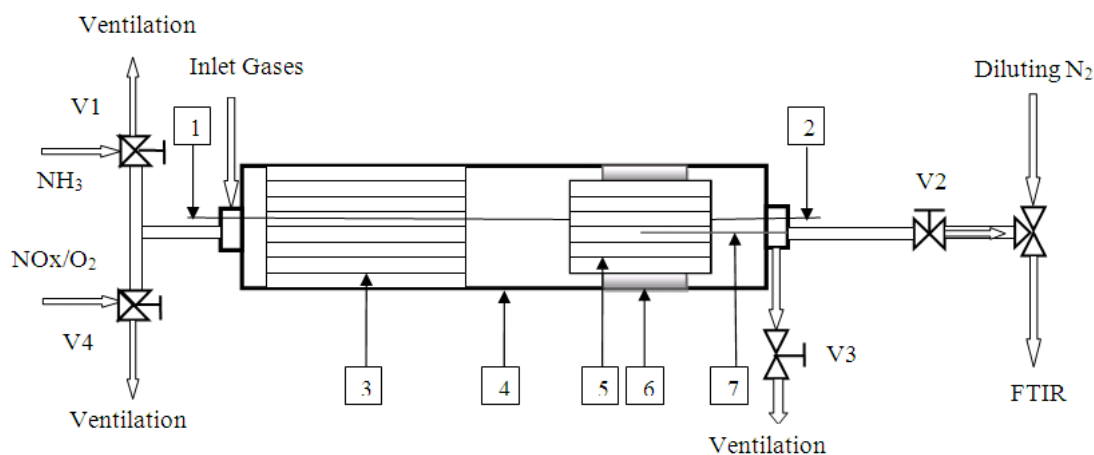


Figure 6.2 NH_3 pulsing adsorption sampling unit: (1) inlet thermocouple, (2) outlet thermocouple, (3) hollow quartz tubes, (4) quartz reactor tube, (5) catalyst monolith, (6) insulation/wrapping material, (7) silica capillary.

To sample the gases along the channel of the monolith, a fused silica capillary was inserted into the desired cell. Care was taken to ensure that the same channel was sampled after each stage of aging to remove any potential issues with maldistribution of washcoat loading in adjacent channels for example. 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 by slightly adjusting the pressure within the reactor. Unless specified, the flow rate in the sampled cell was 44 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.

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 reaction between NO_x/O₂ and NH₃ prior to the catalyst on the upstream stainless steel tubing, they were introduced separately into the reactor. NH₃ and NO_x/O₂ were pulsed into the system, with various pulsing times tested. H₂O and CO₂ concentrations were fixed at 5% and 7%, respectively, with balance N₂. In order to avoid the effect of a delay in mass flow controller responses, NH₃ and NO_x/O₂ were added into the system through V1 and V4 manually, with the two gas mixtures constantly flowing, either into the reactor or to vent. The total gas flow rate through the system was 3.0 L/min, corresponding to a gas hourly space velocity (GHSV) at STP of 30,000 h⁻¹ over the monolithic catalyst volume. However, due to sampling, the flow rate in the tested channel was different from those not being tested. Unless otherwise specified, the normal flow rate through the sampled channel in this paper is 44ml/min, corresponding to a GHSV at STP of 60,000h⁻¹ for the tested channel.

Two categories of experiments were conducted: NH₃ adsorption, and NH₃ adsorption followed by NO/NO_x SCR reaction. In an NH₃ adsorption only process, NH₃ was introduced into the system as a pulse, with pulses lasting from 10 seconds to several minutes. After an NH₃ pulse, NH₃ concentrations along the length of catalyst were monitored with SpaciFTIR by sampling gases at different points along the catalyst channel. For NH₃ adsorption followed by NO/NO_x SCR reaction, NH₃ was first introduced into the system as a pulse, and after a period of time, which is named the “time gap” in this paper, NO or NO + NO₂ were introduced into the system as a pulse as well. After the introduction of NO or NO + NO₂, the concentration of NO and NO₂ were monitored with SpaciFTIR by sampling gases at different points

along the catalyst channel. After each test, the catalyst was cleaned using the fast SCR reaction, followed by sustained flow of N_2 , H_2O and CO_2 to purge the system. The “cleanness” of the catalyst was inspected by monitoring the gas phase composition. When the concentrations of NH_3 , NO and NO_2 along the length of catalyst in the gas phase were known, the quantity of NH_3 adsorbed on the catalyst surface and the quantities of NO and/or NO_2 consumed due to the SCR reactions could be calculated. And vice versa, knowing how much NO or NO_2 was consumed along the length of catalyst allows determination of how much NH_3 was distributed along the length of the catalyst. Ultimately this demonstrates where the NH_3 is adsorbed with changes in pulse parameters, but also if and to what extent NH_3 migrates after the pulse ends.

Keeping the flow rate consistent when sampling at different points along the length of the catalyst is very important to ensure relevant data. The adsorption quantity of NH_3 on the catalyst is calculated based on the change of NH_3 concentration in the gas phase and the gas volume flow rate. The concentration of NH_3 in the gas phase is monitored by FTIR spectroscopy. When the sampling point was moved down the length of the catalyst, if the volume flow rates of the gas phase were not kept consistent throughout the experiment, this inconsistency will affect the adsorption profiles of NH_3 along the length of catalyst. Obviously, the presence of the capillary will affect the flow pattern in the channel. However, it is important to point out that the change in flow pattern after the sampling point had little impact on the adsorption profile. What is being measured is the NH_3 concentration upstream of the sampling point.

The presence of capillary in the channel will increase the resistance to the flow in the channel, which changes when the position of capillary in the channel varies. When the front end of capillary is positioned in the front of the channel, the flow through the annular space between the capillary and the channel wall is less. Therefore, the flow through the capillary, or the sampling amount, is increased in order to keep the total flow through the channel the same. Vice versa, when the sampling point is positioned at the back of the channel, the sampling amount is decreased accordingly. To adjust the sampled amount, the pressure in the reactor is changed, but actually only slightly, by adjusting the flow rate of ventilation through valve V3 in Figure 6.2. The volume flow rates of gases through the annular space between capillary and channel wall when the capillary was positioned at different positions along the channel were estimated by COMSOL, while the sampled amount of gas was monitored with the FTIR via the CO_2 concentration. The inlet concentration of CO_2 was kept the same and there is no formation or consumption of CO_2 in the reaction or system. Therefore, the CO_2 concentration was the measure of how much gas was being sampled. As mentioned before, the normal flow rate through the sampled channel in this paper is 44ml/min. The consistency of the test results indicated that the control of volume flow rate through the channel was acceptable. And as a reminder, the upstream NH_3 trapped is what is measured.

6.3 Results and discussion

6.3.1 NH₃ adsorption profiles

To investigate the effect of NH₃ distribution along the SCR catalyst on the outcome of SCR reactions, a series of NH₃ pulse adsorption experiments were run, varying NH₃ concentration, temperature, and adsorption/pulse time. Understanding how the adsorbed NH₃ distribution profile evolves with time in the process of adsorption can help determine, for example, the length of rich time required for the upstream catalyst to generate enough NH₃ to deposit on the downstream SCR catalyst for subsequent lean operation. The amounts of NH₃ stored on the lightly-aged catalyst as a function of catalyst position and pulse time are shown in Figure 6.3. The NH₃ inlet concentration was fixed at 419 ppm, with the pulse time ranging from 30 to 180 seconds. The adsorbed NH₃ quantity is expressed as the number of moles per unit length of the probed catalyst channel. The data show that when the catalyst was far from being saturated, the amount of NH₃ adsorbed increased almost linearly with the pulse length. When the pulse time was less than 90 seconds, the adsorption profiles have similar slopes/profiles. When the pulse time was greater than 90 seconds, and the adsorbed NH₃ quantity approached the saturation value for that portion of sample, which in this case was about 1.65 μmol/cm at 250°C, the front part of the adsorption profile began to level out. The evolution of the NH₃ adsorption profiles with exposure time is typical of what is observed in sorbent beds. The distribution of adsorbed NH₃ on the catalyst is affected by the concentration as a driving force and adsorption time. As the inlet NH₃ concentration is constant, the adsorption driving force decreases as the quantity of adsorbed NH₃ on the catalyst increases. In comparing the adsorption profiles before and after 90 seconds, it is evident that when the quantity of adsorbed NH₃ on the catalyst was low, the NH₃ adsorbed at early times had little effect on subsequent NH₃ adsorption. However, higher levels of adsorbed NH₃ did slow the rate of NH₃ adsorption. At about 120 seconds, the very front of the catalyst approached saturation. For the case of a 180 second pulse time, more than half of the catalyst channel was saturated. With increasing surface coverage, the adsorption driving force of course decreased, which led to the NH₃ slip even though the whole catalyst was not saturated. When the pulse time was less than 120 seconds, there was no significant NH₃ slip observed. However, with longer pulse times, NH₃ slip was apparent.

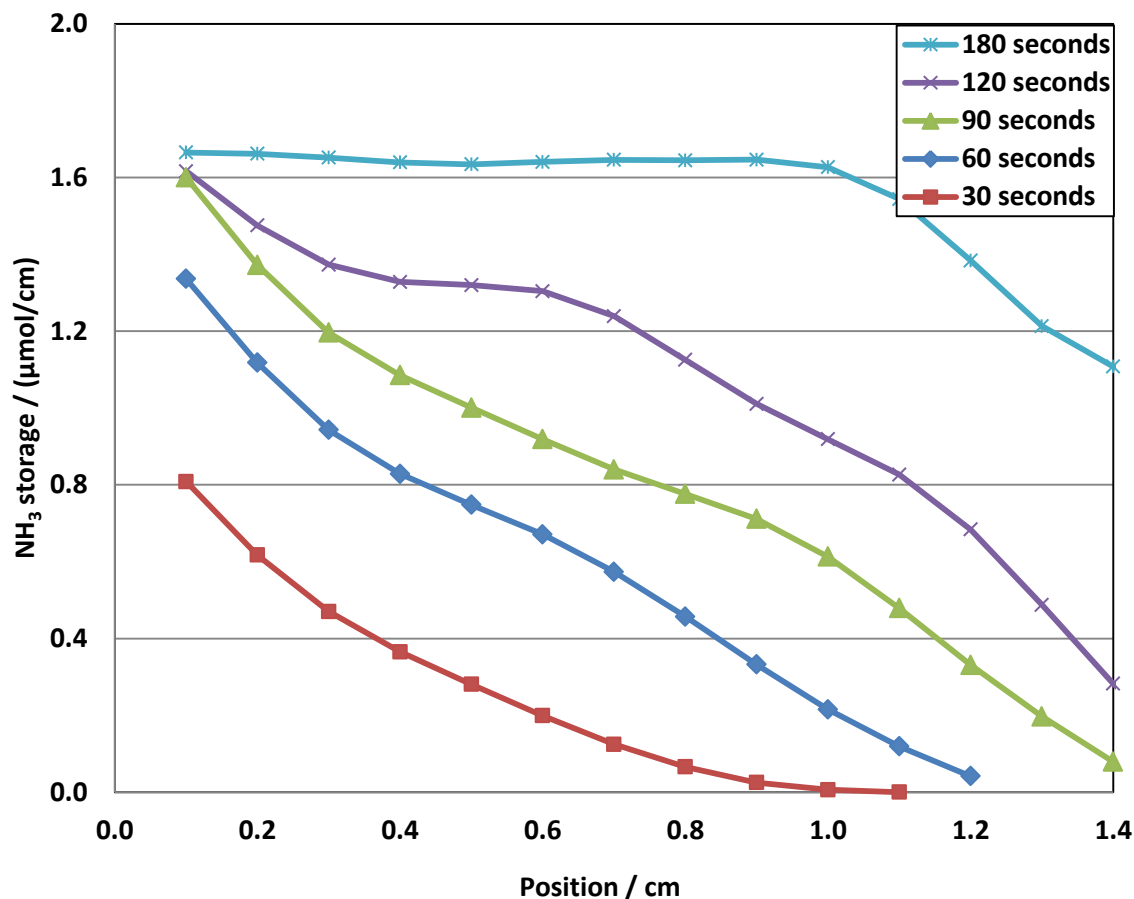


Figure 6.3 NH_3 adsorption profiles as a function of NH_3 exposure time; conditions: 250°C ; lightly aged catalyst; NH_3 inlet concentration = 419 ppm.

To evaluate the effect of NH_3 inlet concentration versus pulse time (for the same ultimate amount of NH_3 added), NH_3 inlet concentrations and pulse times were varied accordingly, and the data are shown in Figure 6.4. For a shorter pulse time, the NH_3 inlet concentration was higher; for a longer pulse time, a lower NH_3 inlet concentration was used. The effect of the total amount was also evaluated and because the flow rates were the same for all the tests, the product of pulsing time and NH_3 inlet concentration is proportional to the quantity of introduced NH_3 , with a ratio of 3:2:1 for the tests run. For the largest amount of NH_3 introduced, the NH_3 adsorption profiles were very similar. However, for the two with lesser amounts of NH_3 introduced, there were differences evident between the NH_3 adsorption profiles. In these with less NH_3 input, the adsorption profiles associated with the higher NH_3 inlet concentration and shorter pulsing time were steeper than the adsorption profiles associated with lower NH_3 inlet concentration and longer pulse time. These results indicate that the extent of NH_3 adsorption is a concentration driven process toward the beginning of adsorption, i.e. away from saturation. Of course,

with a higher NH_3 inlet concentration, there will be a higher adsorption rate. On the other hand, the driving force also depends on the surface NH_3 concentration, where a maximum exists. At the beginning of the NH_3 pulsing adsorption process, the catalyst was clean and there was no NH_3 on the solid surface and therefore, the NH_3 adsorption rate is purely dependent on the NH_3 inlet concentration. And of course as the surface concentration increases, the driving force for adsorption decreases.

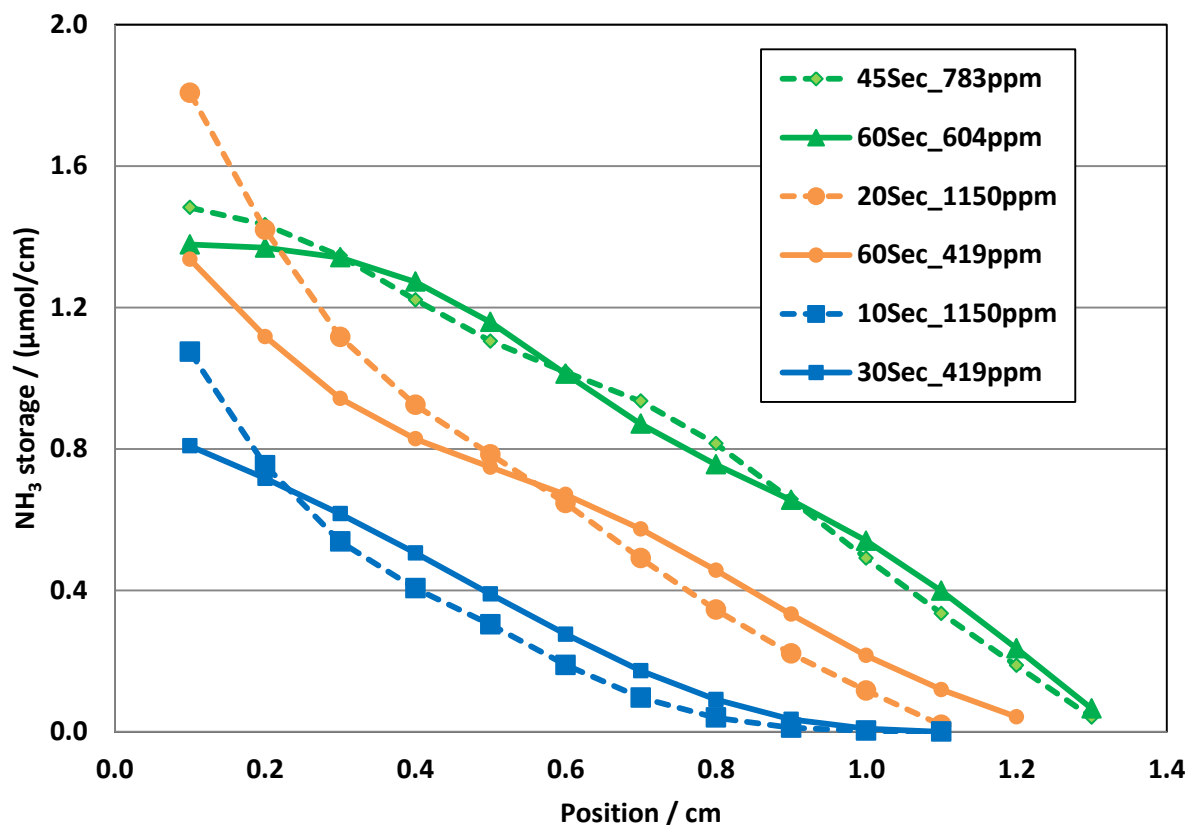


Figure 6.4 Effects of NH_3 concentration and pulsing time on NH_3 adsorption profiles; conditions: 250°C; lightly aged catalyst.

Thus, with a higher inlet concentration, and shorter time, the adsorption profile is sharper, resulting in a “crossover” in adsorbed amounts, with more stored in the back of the catalyst with smaller inlet concentrations and longer time. With a larger driving force for NH_3 adsorption at the onset of the dose when a larger inlet NH_3 concentration was used, more adsorbed at the inlet section. Then since more was adsorbed upstream, less was available for downstream sites, resulting in the sharper gradient. With a smaller inlet concentration, the driving force is smaller, leading to less adsorbed at the inlet section, but more available for downstream locations and more adsorbed downstream.

Regarding the effect of catalyst aging on NH_3 adsorption profiles, comparison tests were done on the lightly and highly aged catalysts for two sets of inlet conditions at 250°C. NH_3 adsorption profiles are shown in Figure 6.5. Compared with the NH_3 adsorption profiles on the lightly aged catalyst, the profiles

along the highly aged catalyst were flatter, indicating that catalyst aging caused a reduction in NH_3 storage. Coincidentally, more NH_3 was therefore available for adsorption at the back of the catalyst, resulting in a flatter NH_3 storage profile. Relative to the lightly aged catalyst, similar trends as a function of NH_3 inlet concentration were observed. When the NH_3 quantity was significantly less than the quantity needed to saturate the front part of the catalyst, a higher NH_3 inlet concentration resulted in a steeper NH_3 adsorption profile.

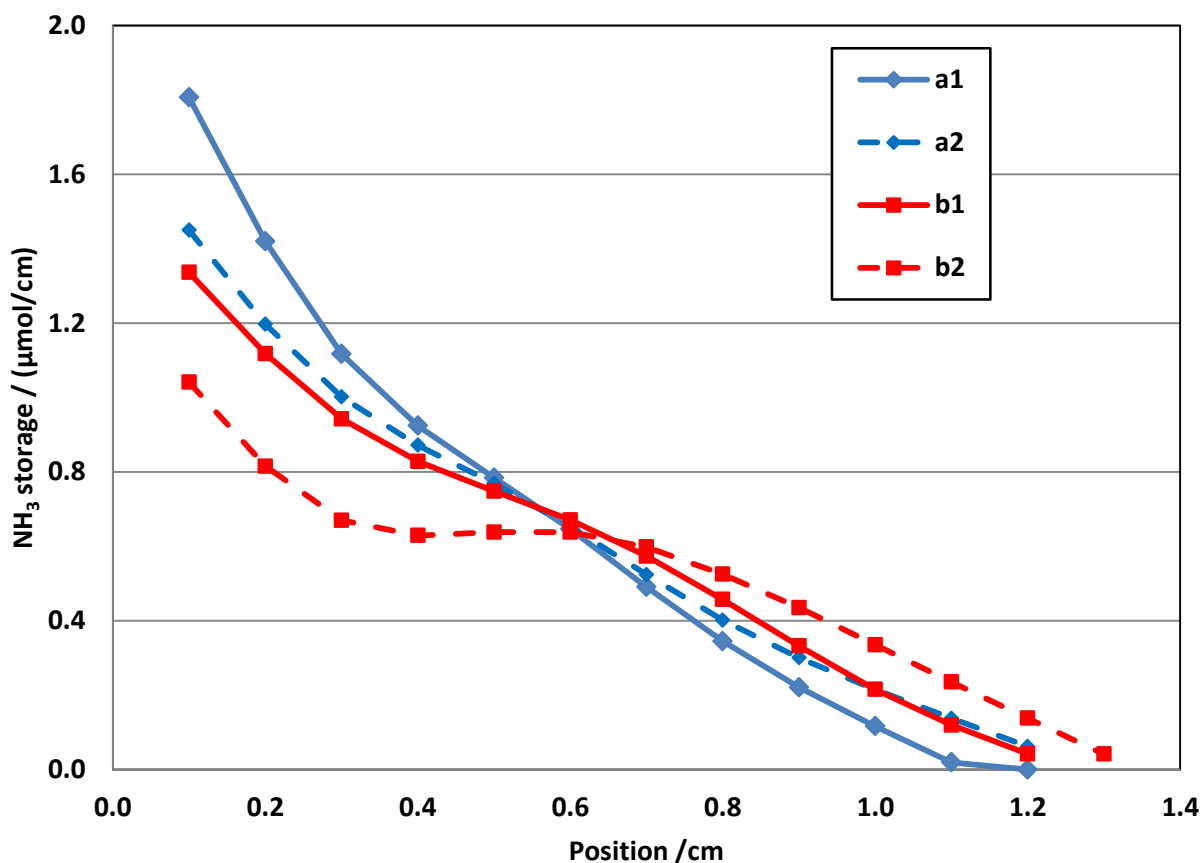


Figure 6.5 Effect of aging on NH_3 adsorption profiles; conditions: 250°C; pulsing time in seconds $\times$ NH_3 inlet concentration in ppm: a1:20 $\times$ 1150 with the lightly aged catalyst; a2: 20 $\times$ 1150 with the highly aged catalyst; b1:60 $\times$ 419 with the lightly aged catalyst; b2: 60 $\times$ 419 with the highly aged catalyst.

The effects of temperature on the NH_3 storage profile on the lightly aged catalyst for three pulsing times were evaluated at 250°C and 300°C and are shown in Figure 6.6. The data at both temperatures indicate that when the pulsing time is about 120 seconds, the very front of the catalyst approached saturation. With a 180 second pulse, the front part of the catalyst saturated. The amount for saturation at 300°C was about 1.5 $\mu\text{mol/cm}$, less than that at 250°C. With less required for saturation, this also demonstrates that when temperature is increased, the NH_3 adsorption profiles will become flatter. As the adsorption capacity decreased with increased temperature, more NH_3 was available at the back of the catalyst for adsorption.

This ultimately resulted in more NH_3 at the back of the catalyst, for conditions that do not approach full saturation.

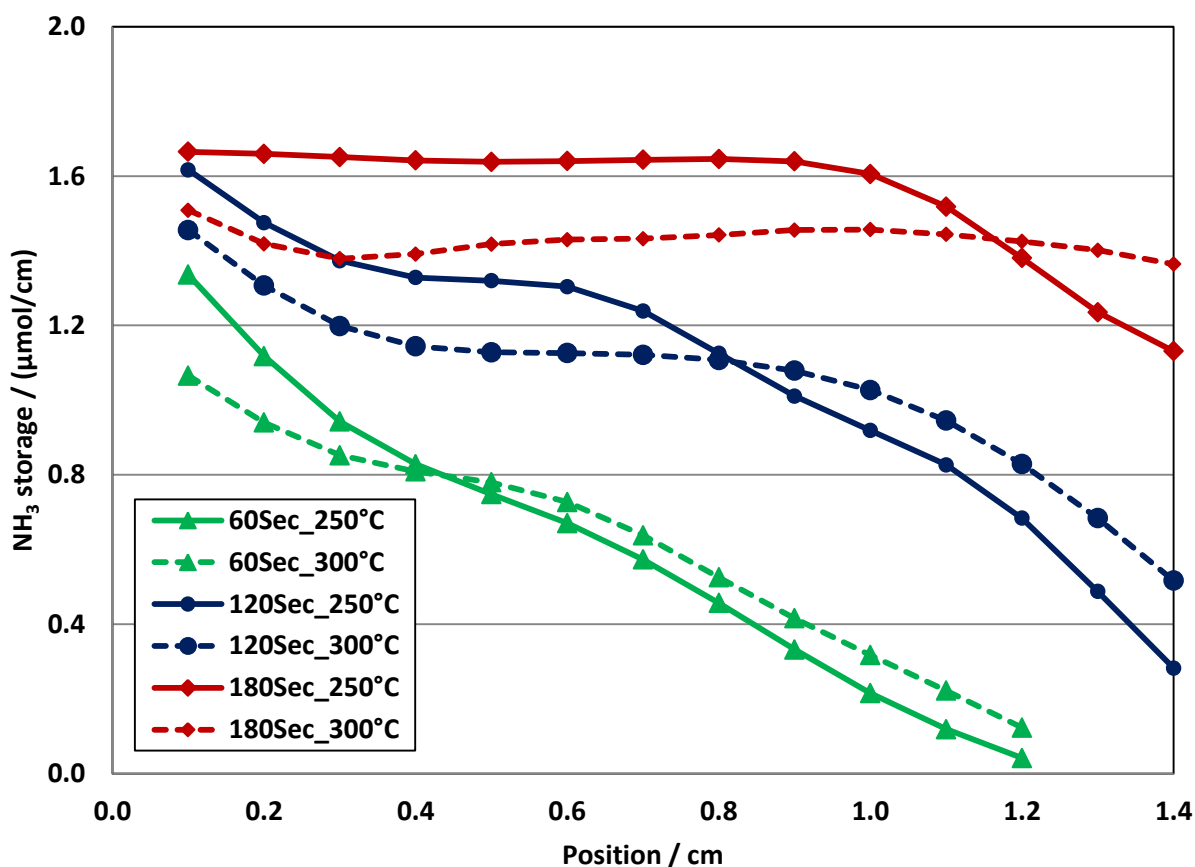


Figure 6.6 Effect of temperature on NH_3 adsorption profiles; conditions: lightly aged catalyst; NH_3 inlet concentration: 419 ppm.

6.3.2 NH_3 migration after adsorption

For the application of a passive SCR system, understanding the adsorption profiles is critical, and not only with the introduction of the pulse, but what happens afterwards, prior to NO_x reaching the downstream catalyst. Of key interest is NH_3 migration along the SCR catalyst prior to, or during NO_x exposure. NH_3 adsorption and desorption can occur along the monolith, analogous to what occurs in a gas chromatograph column. And, even with NO_x present, NH_3 migration may still be occurring as NO_x is consumed upstream. The differences between the NO_x consumption profiles and NH_3 pulse adsorption profiles can be used to evaluate NH_3 migration within the time gap between the NH_3 pulse ending and the SCR reaction beginning.

The fast SCR reaction was used to characterize NH_3 migration. Factors such as time gap, temperature, and catalyst aging on NH_3 migration were investigated. Assuming the SCR reactions follow standard and/or fast SCR reaction mechanisms [88, 94, 158], from the consumption of NO_x the NH_3 amounts

along the length of catalyst can be determined, based on where the SCR reactions occurred. To evaluate the NH_3 distribution profiles after migration, NO and NO_2 were introduced into the system in a 1:1 ratio after an NH_3 pulse. NO and NO_2 concentrations along the length of catalyst were measured with SpaciFTIR, from which the NOx consumption profiles were obtained. With the fast SCR reaction, the NOx and NH_3 consumption ratio is 1:1.

For these tests, the NH_3 inlet concentration was kept constant (1150 ppm) as was the NH_3 pulse time (20 seconds). The inlet concentration of NOx was 416 ppm, with a pulse time of 60 seconds. The total NH_3 dose was slightly less than that of NOx. In addition, due to NH_3 desorption after adsorption, some of the NH_3 would exit the reactor during the time gap and NOx pulse.

The effects of the time gap on NH_3 migration were investigated and the NOx consumption results obtained with the highly aged catalyst are shown in Figure 6.7(a). As the time gap increased, the NOx consumption profile leveled out. With a time gap greater than 30 seconds, the profiles were quite similar demonstrating that no significant NH_3 migration occurred after a 30 second delay. Based on the dramatic change in the NOx consumption profiles within the first ten seconds, NH_3 migration was very significant just after the NH_3 pulse ended. However, with increasing time between NH_3 ending and NOx entering, NH_3 migration became less significant. These data suggest that there were weakly and strongly adsorbed NH_3 species on the catalyst surface. The weakly adsorbed NH_3 migrated easily, while the strongly adsorbed NH_3 did not migrate significantly.

Weakly and strongly adsorbed NH_3 have been observed/described previously [6, 130]. It is generally agreed that NH_3 can be adsorbed on both Lewis and Brønsted acidic sites. When it is adsorbed through a Lewis-type interaction, it takes the form of molecularly adsorbed NH_3 while over Brønsted acidic surface hydroxyl groups, ammonium ions are formed. Lietti et al [192] found, however, that when NH_3 is protonated as a NH_4^+ ion over Brønsted sites, it is thermally less stable than the molecularly coordinated species. The results observed as part of this paper are supported by the aforementioned observations, which claim that there are weak and strong adsorption sites for NH_3 on zeolite catalysts.

The presence of reaction at the outlet portion, exceeding the amount of NH_3 that was originally stored, indicates migration, but not only was there NH_3 migration; there was also loss of NH_3 from the system. This can be described by an integral NOx consumption along the length of the catalyst, which is shown in Figure 6.7(b). These data indicate that a significant amount of NH_3 was lost when the time gap was as low as five seconds. Some NH_3 migrated from the front of the catalyst to the back of the catalyst, and was still available for SCR. With increasing time, the integral NOx consumption profiles tended to converge. As the gap time exceeded 40 seconds, NH_3 migration was not significant and the total NOx consumption did not change significantly. It is clear that adsorbed NH_3 migrated down the channel immediately after adsorption (when the gas-phase NH_3 is absent). For weakly adsorbed NH_3 , the effect of migration was

fast and significant. One way to possibly take advantage of this is to reserve some length of the channel toward the catalyst outlet to capture the desorbed NH_3 from the front part of the catalyst, thus decreasing the required amount of rich time to generate NH_3 . Another conclusion that can be drawn from these observations is that both weakly and strongly adsorbed NH_3 can readily react with NO or NO_x .

Regarding the effect of catalyst aging on NH_3 migration and loss, similar experiments were done with the lightly aged catalyst at 250°C , with time gaps of 10 and 70 seconds. The NO_x consumptions per unit length of catalyst over the lightly and highly aged catalysts were measured (but not shown here for brevity). The conditions for NH_3 and NO_x pulsing were the same as those described in Figure 6.7(a). As discussed above, aging results in less NH_3 adsorption and thus the adsorption profiles were more even along the length of catalyst. And as would be expected, the NO_x consumption profiles for the highly aged catalyst were also flatter.

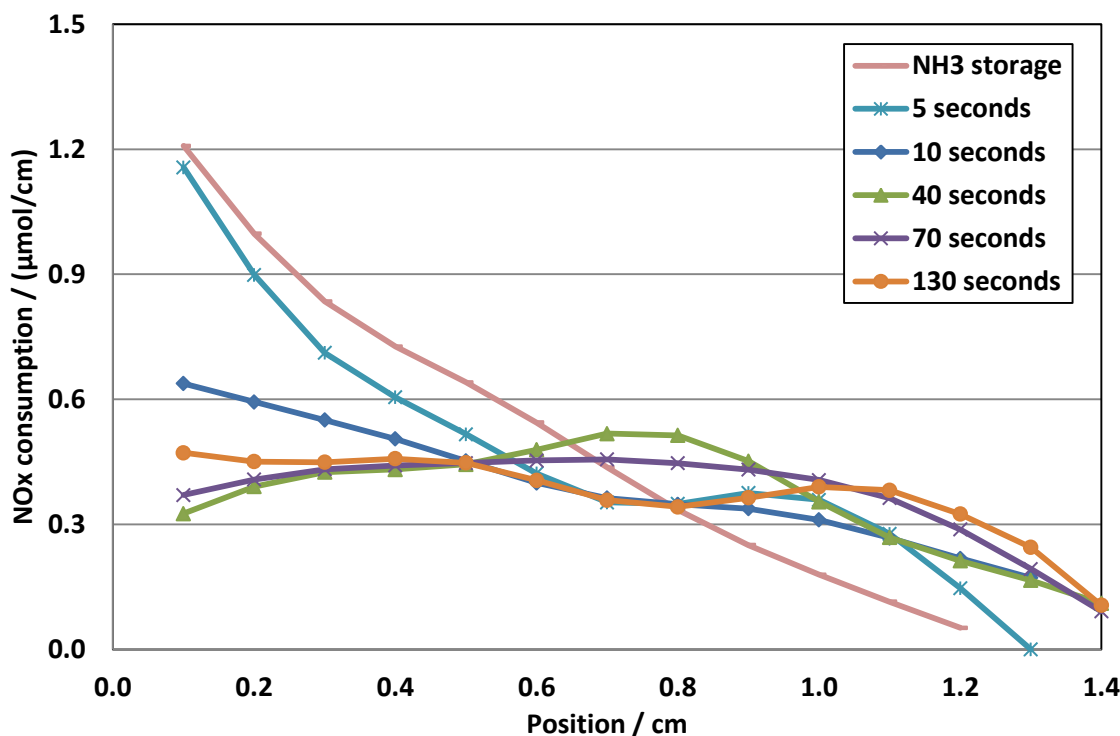


Figure 6.7(a) NH_3 migration after adsorption: effect of time gap: conditions: 250°C ; highly aged catalyst; NH_3 inlet concentration: 1150 ppm; NH_3 pulsing time: 20 seconds; NO_x inlet concentration: 416 ppm; $\text{NO}:\text{NO}_2 = 1:1$; NO_x pulsing time: 60 seconds.

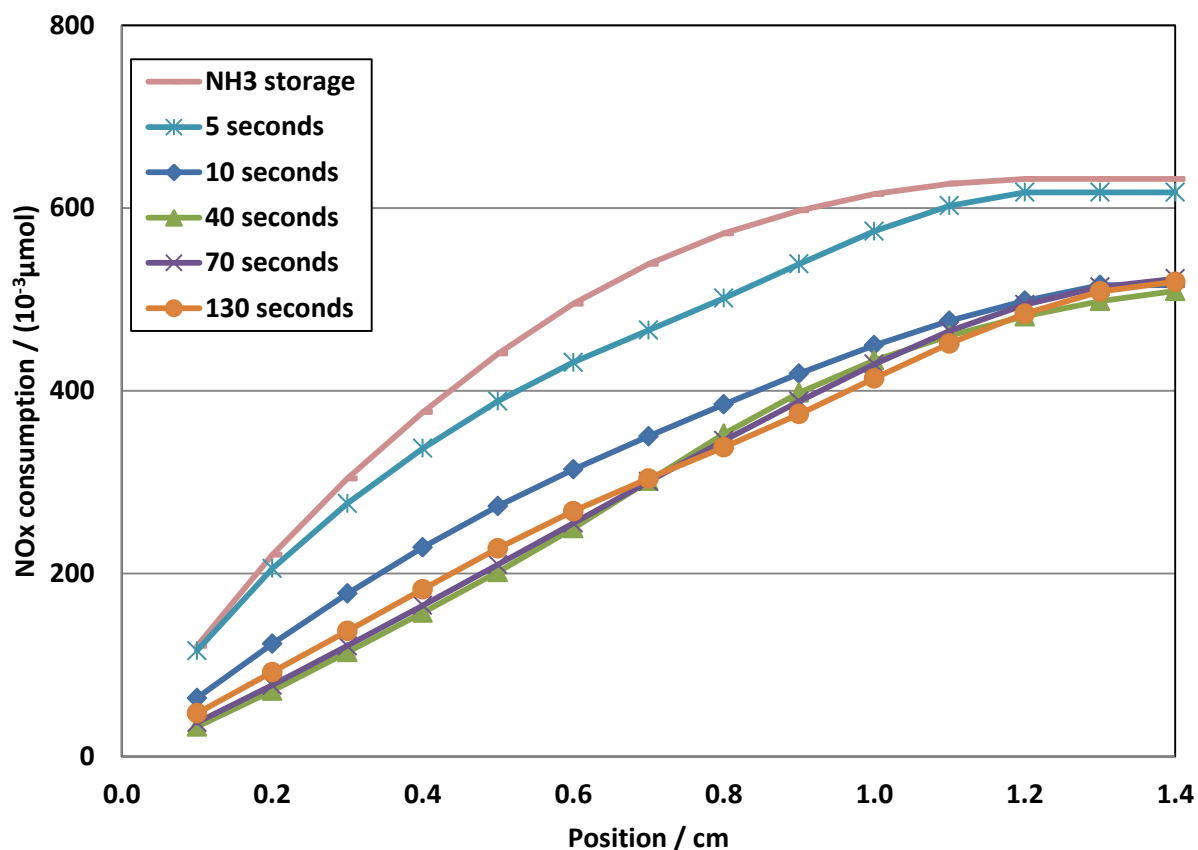


Figure 6.7(b) Effect of time gap on NH_3 loss due to migration; conditions: 250°C ; highly aged catalyst; NH_3 inlet concentration: 1150 ppm; NH_3 pulsing time: 20 seconds; NO_x inlet concentration: 416 ppm; $\text{NO}:\text{NO}_2 = 1:1$; NO_x pulsing time: 60 seconds.

The effect of catalyst aging on the amount of NH_3 that desorbed and did not re-adsorb is shown in Figure 6.8, where the integral NO_x consumption along the length of the catalyst is shown. The data show that there was no significant difference between the highly and lightly aged catalysts for the 70-second time gap, which indicates that catalyst aging did not lead to a significant difference in the storage and migration of strongly adsorbed NH_3 . However, again, at the shorter time gap times, there was a difference, which demonstrates that the weakly adsorbed NH_3 is affected by thermal aging.

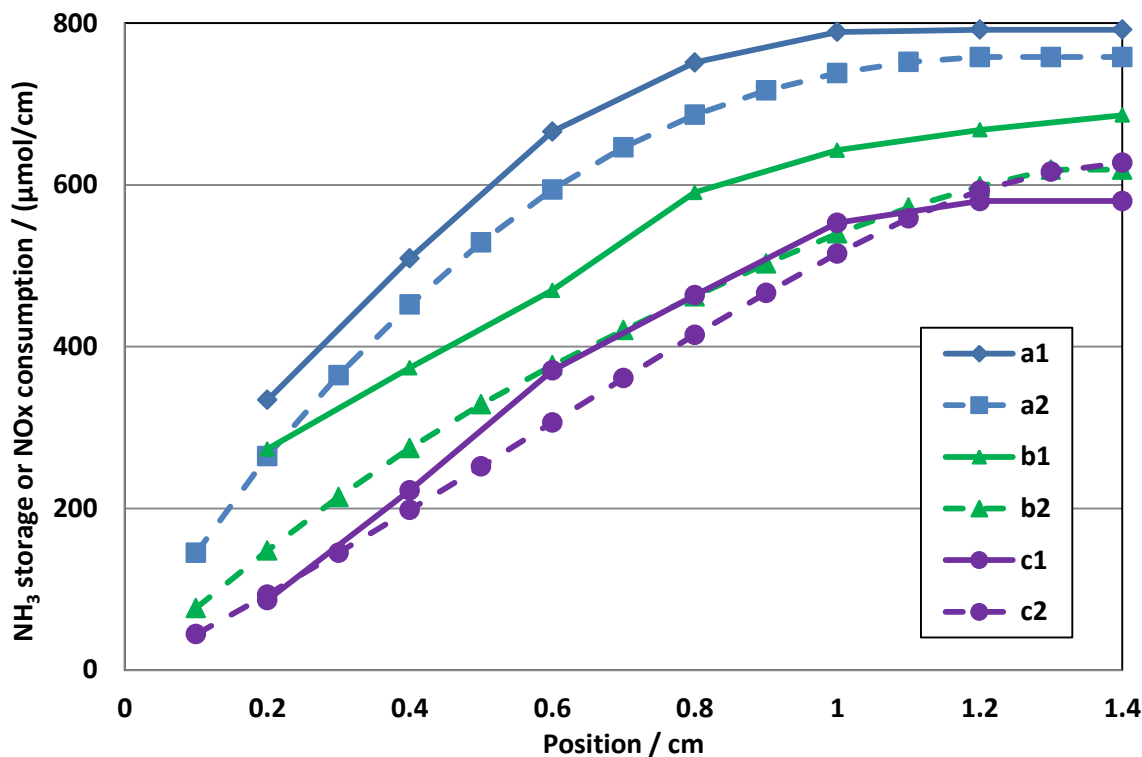


Figure 6.8 Effect of catalyst aging on NH_3 loss; conditions: 250°C ; NH_3 inlet concentration: 1150 ppm; NH_3 pulsing time: 20 seconds; NO_x inlet concentration: 416 ppm; $\text{NO}:\text{NO}_2 = 1:1$; NO_x pulsing time: 60 seconds; a1: NH_3 storage on lightly aged catalyst; a2: NH_3 storage on highly aged catalyst; b1: time gap 10 seconds on lightly aged catalyst; b2: time gap 10 seconds on highly aged catalyst; c1: time gap 70 seconds on lightly aged catalyst; c2: time gap 70 seconds on highly aged catalyst.

The effect of temperature on NH_3 migration and loss was also evaluated. The density and integral functions of NO_x consumption were compared at 250°C and 300°C , with integral results shown in Figure 6.9. The data demonstrate that increased temperature enhanced NH_3 migration, which is supported by literature TPD experiment observations where NH_3 desorption is typically observed at temperatures greater than 200°C . [68] The figure also shows that there was no significant change in the loss of strongly adsorbed NH_3 ; however, the loss of weakly adsorbed NH_3 was faster at higher temperature. The observation that the loss of strongly adsorbed NH_3 is less than that of weakly adsorbed NH_3 could be a kinetic effect with the desorption rate being quite small for strongly adsorbed NH_3 . The time gaps in these tests were relatively short, but applicable. It is possible that with longer time gaps used some more significant migration of the more strongly adsorbed species may have been observed, but here the effect of temperature indicates it is weakly adsorbed NH_3 that is affected.

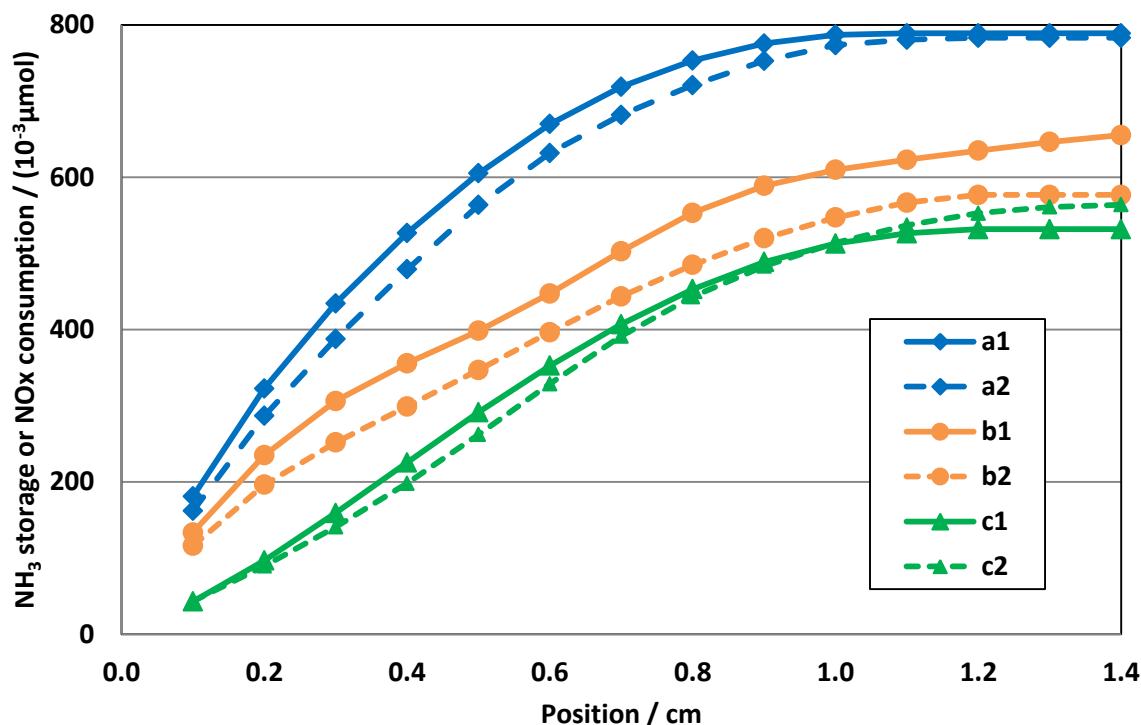


Figure 6.9 Effect of catalyst aging on NH_3 loss; conditions: lightly aged catalyst; NH_3 inlet concentration: 1150 ppm; NH_3 pulsing time: 20 seconds; NO_x inlet concentration: 416 ppm; $\text{NO} : \text{NO}_2 = 1:1$; NO_x pulsing time: 60 seconds; a1: NH_3 storage at 250°C ; a2: NH_3 storage at 300°C ; b1: time gap 10 seconds at 250°C ; b2: time gap 10 seconds at 300°C ; c1: time gap 70 seconds at 250°C ; c2: time gap 70 seconds at 300°C .

6.3.3 Standard and fast SCR reactions with the SCR catalyst pre-covered with NH_3

With the NH_3 adsorption profiles and migration known, SCR reactions on NH_3 pre-covered samples, with different profiles, can be evaluated. The fast SCR reaction was conducted and with SpaciFTIR, the concentrations of NO and NO_2 along the length of the catalyst channel were measured and the consumption profiles of NO and/or NO_2 were obtained. In the experiments, NH_3 was first introduced into the system as a pulse. After a time gap of ten seconds, NO and NO_2 , with a 416 ppm total concentration and ratio of 1:1, were introduced into the system. NO_x consumption data along the catalyst are shown in Figure 6.10.

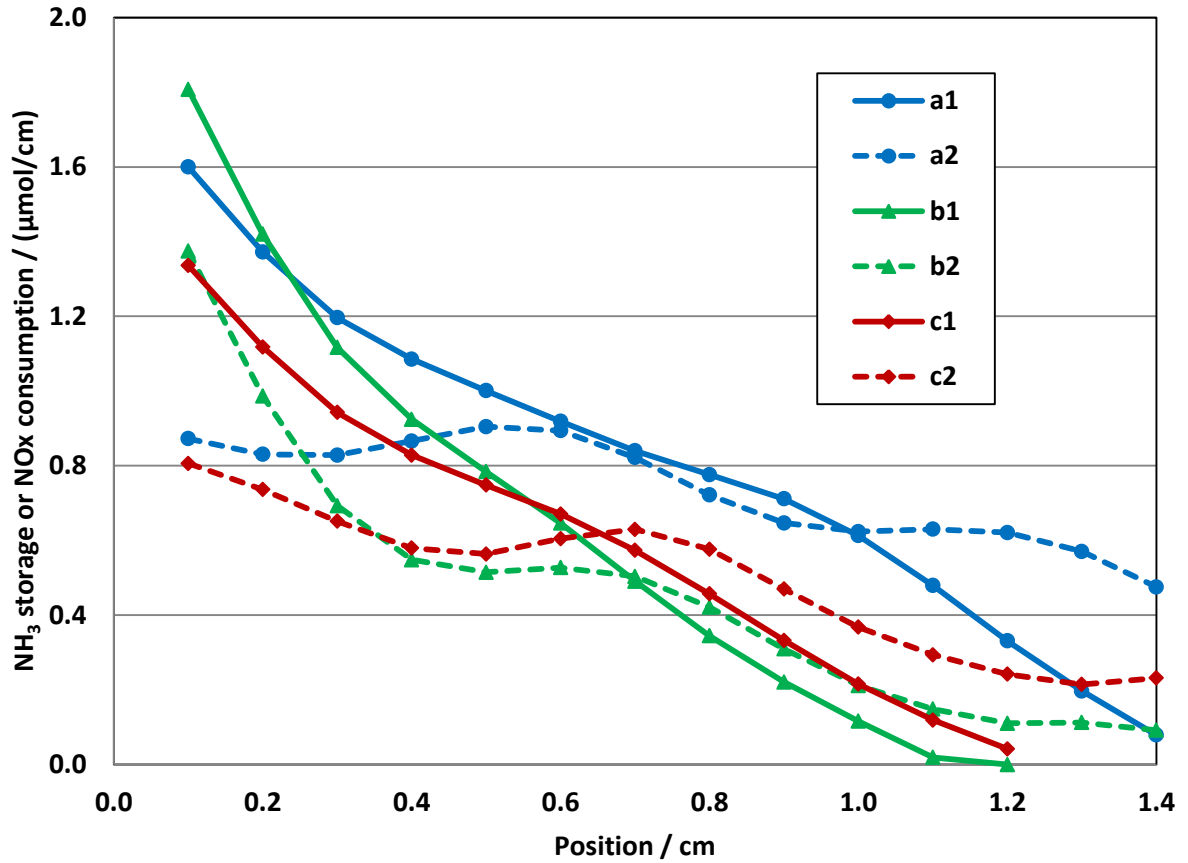


Figure 6.10 Comparison between NH_3 adsorption profiles and NO_x consumption profiles under fast SCR reaction conditions; test conditions: 250°C ; lightly aged catalyst; NO_x inlet concentration during the NO_x pulse: 416 ppm; $\text{NO}:\text{NO}_2 = 1:1$; time gap between NH_3 pulsing adsorption and SCR reactions 10 seconds; a1: NH_3 storage with 90 seconds pulsing time and a 419 ppm NH_3 inlet concentration; a2: NH_3 storage with 90 seconds pulsing time and 419 ppm NH_3 inlet concentration followed by a 90 second NO_x pulse; b1: NH_3 storage with 20 seconds pulsing time and an 1150 ppm NH_3 inlet concentration; b2: NH_3 storage with 20 seconds pulsing time and an 1150 ppm NH_3 inlet concentration followed by a 60 second NO_x pulse; c1: NH_3 storage with 60 seconds pulsing time and a 419 ppm NH_3 inlet concentration; c2: NH_3 storage with 60 seconds pulsing time and a 419 ppm NH_3 inlet concentration followed by a 60 second NO_x pulse.

For the same reasons discussed above, the data from all three groups of comparisons showed that NO_x consumption profiles along the length of catalyst were flatter than their corresponding NH_3 pulsing adsorption profiles. In the front part of the catalyst, NO_x consumption quantities were less than the

amount of NH_3 adsorbed during the NH_3 pulse; while in the back of the catalyst, NO_x consumption quantities were higher than those of the amount of NH_3 adsorbed. Regarding the effect of NH_3 input quantity, the slope difference between the NH_3 adsorption profile and NO_x consumption profile for larger NH_3 input quantity was more significant than that for a smaller NH_3 input quantity. With more NH_3 adsorbed, NH_3 migration was more significant because the front part of the catalyst was nearer saturation. Also, for the low NH_3 concentration, longer time pulse, there is more chance for migration as well, which would further make the NO_x consumption profile flatter.

In order to determine how standard SCR responds to pre-adsorbed NH_3 , in comparison to fast SCR described above, experiments were run with just NO as well. After NH_3 adsorption, corresponding to the aforementioned fast SCR reaction experiments, the standard SCR reaction was investigated on the lightly aged catalyst with two pulsing conditions. NH_3 with an inlet concentration of 419 ppm was introduced into the system with pulsing times of 60 and 90 seconds. After the NH_3 pulse, NO was introduced into the system 10 seconds later. The pulse times for NO were 60 and 90 seconds. The data, not displayed here, shows that the profiles of NO and NO_x consumption over a unit length of catalyst were similar. The data in Figure 6.11 show the integral NO/ NO_x consumption, which clearly demonstrate that the difference between standard and fast SCR reactions over the SCR catalyst pre-covered with the similar distribution of NH_3 was not significant.

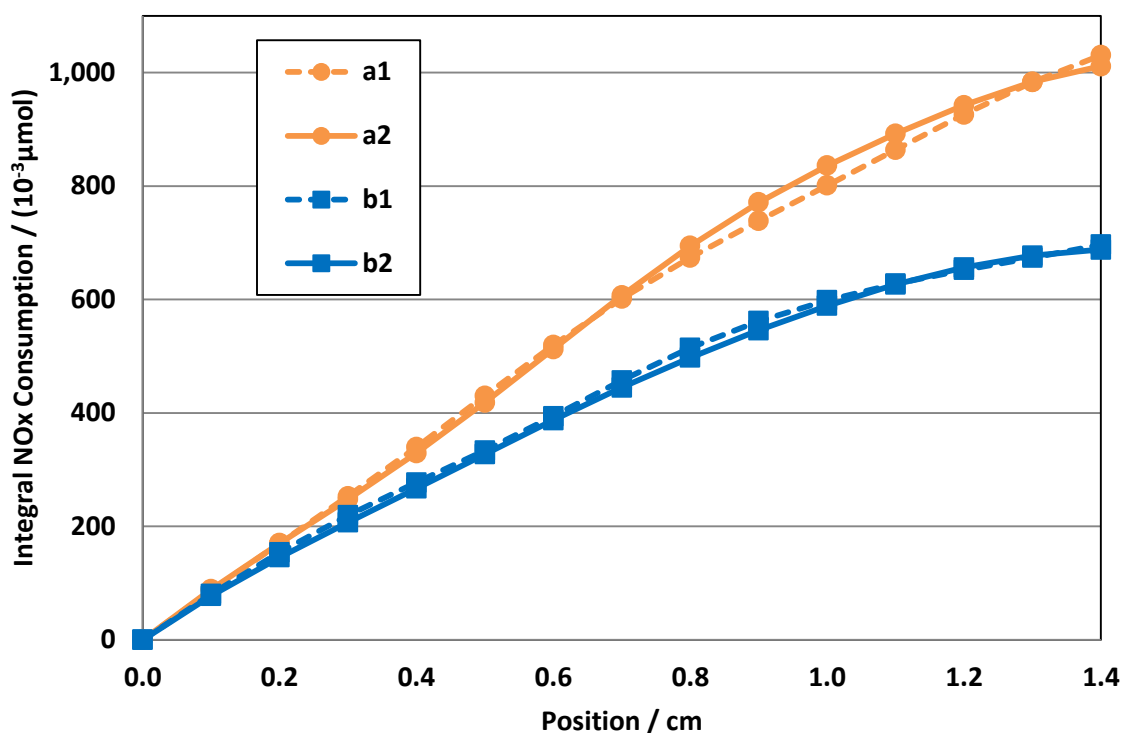


Figure 6.11 NO_x consumption as a function of positions under fast and standard SCR reactions over a SCR catalyst pre-covered with NH₃; conditions: 250°C; lightly aged catalyst; NH₃ inlet concentration: 419 ppm; NO_x inlet concentration: 416 ppm; time gap between NH₃ pulsing adsorption and NO or NO_x pulse: 10 seconds;

a1: 90 seconds NH₃ pulse adsorption followed by 90 seconds 1:1 NO:NO₂ pulse;

a2: 90 seconds NH₃ pulse adsorption followed by 90 seconds NO pulse;

b1: 60 seconds NH₃ pulse adsorption followed by 60 seconds 1:1 NO:NO₂;

b2: 60 seconds NH₃ pulse adsorption followed by 60 seconds NO pulse.

The effects of aging on standard and fast SCR reactions at 250°C were also investigated and compared. The NO consumption profiles along the length of catalyst on the lightly aged catalyst were steeper than those on the highly aged catalyst. This trend was explained above – there is less NH₃ adsorbed along the highly aged catalyst, thus spreading the adsorption profile along the catalyst length. Similar data were obtained for fast SCR reaction conditions. The effects of catalyst aging on NO or NO_x consumption did show a dependence on the relative ratio of NO or NO_x to NH₃, as shown in Figure 6.12. When NO and NO_x pulsing times were 30 seconds, the conversions of NO and NO_x on the lightly and highly aged catalysts were similar. When NO and NO_x pulsing times were 60 seconds, the conversions of NO or NO_x on the lightly aged catalyst were higher than those on the highly aged catalyst. These phenomena indicate

that catalyst aging reduced catalyst activity, as would be expected. When there was enough NH_3 on the catalyst and NO or NO_x was not in large quantity, NO or NO_x could be reduced and decreased catalyst activity was not detected. However, when NO or NO_x was in relatively large quantity, decreased catalyst activity was observed. This may suggest that the reduction of SCR activity over the aged catalyst may be associated primarily with the reduced amount of stored NH_3 . In last section it was concluded that both weakly and strongly adsorbed NH_3 can react with NO_x . Although aging has little effect on the quantity of strongly adsorbed NH_3 , the loss of weakly adsorbed NH_3 can affect the reduction capability of the catalyst. It's been suggested by Ramis et al [56] that both Brønsted and Lewis acid sites can be active centers for SCR reactions on zeolite catalysts. Olsson et al [131] proposed four kinds of active site for NH_3 adsorption on a Cu-ZSM-5 catalyst. The data here do not demonstrate that NH_3 storage is the degradation effect, but do suggest that it plays a role, as would be expected.

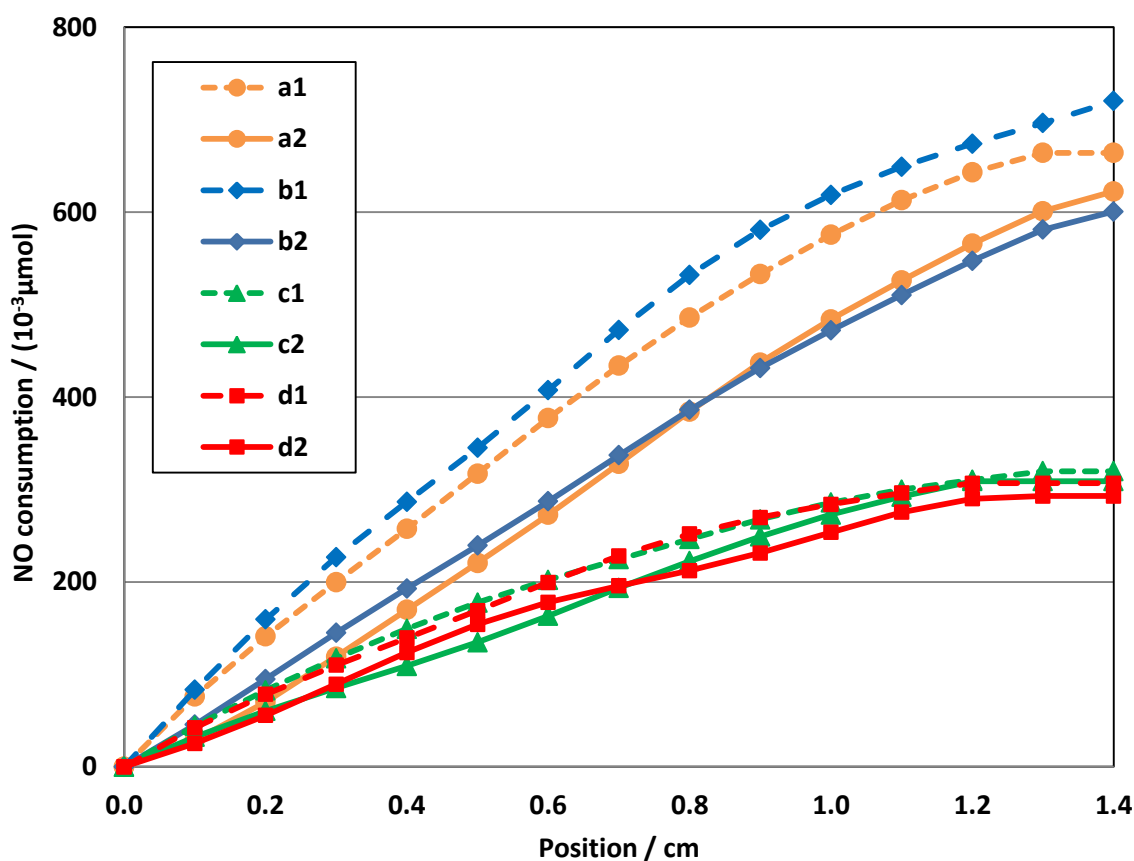


Figure 6.12 Effect of aging and NH_3/NO_x ratio on the fast and standard SCR reactions; conditions: 250°C ; NH_3 inlet concentration: 419 ppm; NO_x inlet concentration: 416 ppm; time gap between NH_3 pulsing adsorption and NO pulse: 10 seconds;

a1: 60 seconds NH_3 pulse adsorption followed by a 60 second NO pulse on lightly aged catalyst;

a2: 60 seconds NH_3 pulse adsorption followed by a 60 second NO pulse on highly aged catalyst;

b1: 60 seconds NH_3 pulse adsorption followed by a 60 second NO_x (1:1 $\text{NO}:\text{NO}_2$) pulse on lightly aged catalyst;

b2: 60 seconds NH_3 pulse adsorption followed by a 60 second NO_x (1:1 $\text{NO}:\text{NO}_2$) pulse on highly aged catalyst;

c1: 60 seconds NH_3 pulse adsorption followed by a 30 second NO pulse on lightly aged catalyst;

c2: 60 seconds NH_3 pulse adsorption followed by a 30 second NO pulse on highly aged catalyst;

d1: 60 seconds NH_3 pulse adsorption followed by a 30 second NO_x (1:1 $\text{NO}:\text{NO}_2$) pulse on lightly aged catalyst;

d2: 60 seconds NH_3 pulse adsorption followed by 30 seconds NO_x (1:1 $\text{NO}:\text{NO}_2$) pulse on highly aged catalyst.

To investigate the effect of NH_3 storage on SCR reactions, different quantities of NH_3 were adsorbed on the catalyst first, and then fixed amounts of NO or NO_x were introduced into the system. NH_3 adsorption and SCR reactions were conducted at 250°C . NO/NO_x consumptions per unit length of catalyst are shown in Figure 6.13(a) and the cumulative of NO/NO_x consumption along the length of catalyst are shown in Figure 6.13(b). In Figure 6.13(a), the data from the test with high NH_3 coverage are similar to those with low NH_3 coverage. So, for the two levels of NH_3 coverage, there was no significant difference between NO/NO_x consumption when the NO and NO_x introduced were less than the quantity of adsorbed NH_3 . The resemblance of NO and NO_x consumption over different levels of NH_3 coverage can be seen more clearly in Figure 6.13(b).

To investigate the effect of temperature on SCR reactions on a catalyst pre-covered with NH_3 , two sets of tests were done at 250°C and 300°C under standard SCR reactions. The density and integral functions of NO consumption along the length of the catalyst are compared (data not displayed). The experiment results showed that when the input quantity of NO was close to that of the adsorbed NH_3 , the NO consumption profile at 300°C was flatter than that at 250°C . However, when the input quantity of NO was less than that of NH_3 adsorbed, the NO consumption trends at 250°C and 300°C were similar, as was the case for data shown in Figure 6.13. Thus, the significance of the effect of temperature on NO consumption depends on the ratio of NO input to NH_3 adsorbed, as expected. Again, this difference is due to the effect of temperature on NH_3 migration. As discussed above, NH_3 migration was more significant at high temperature.

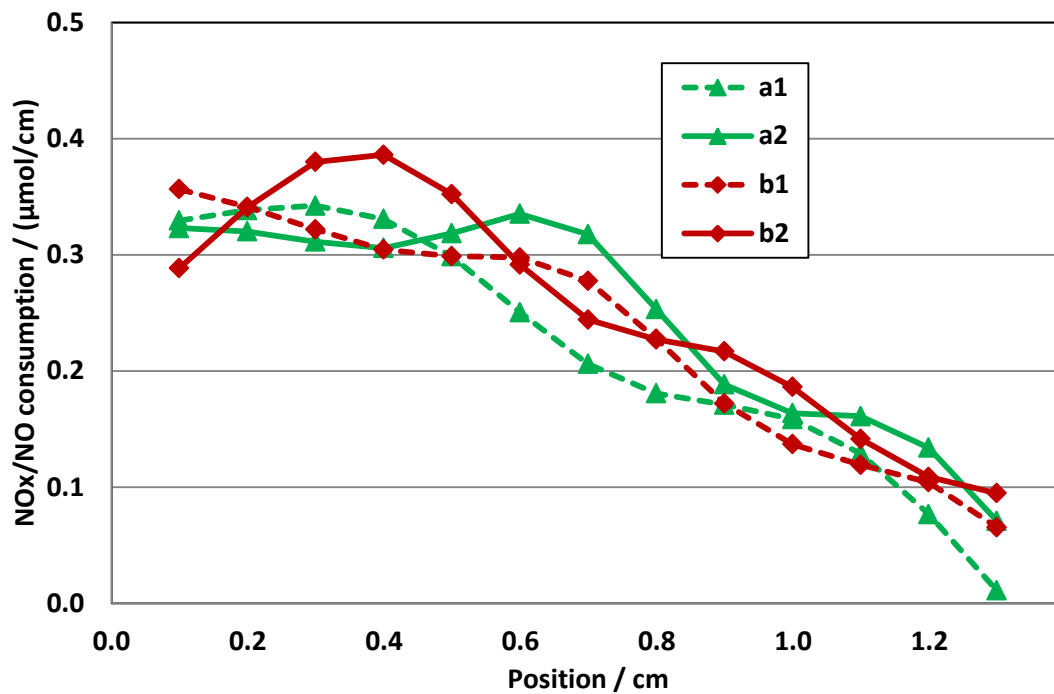


Figure 6.13(a). Effect of NH_3 storage on the standard and fast SCR reactions

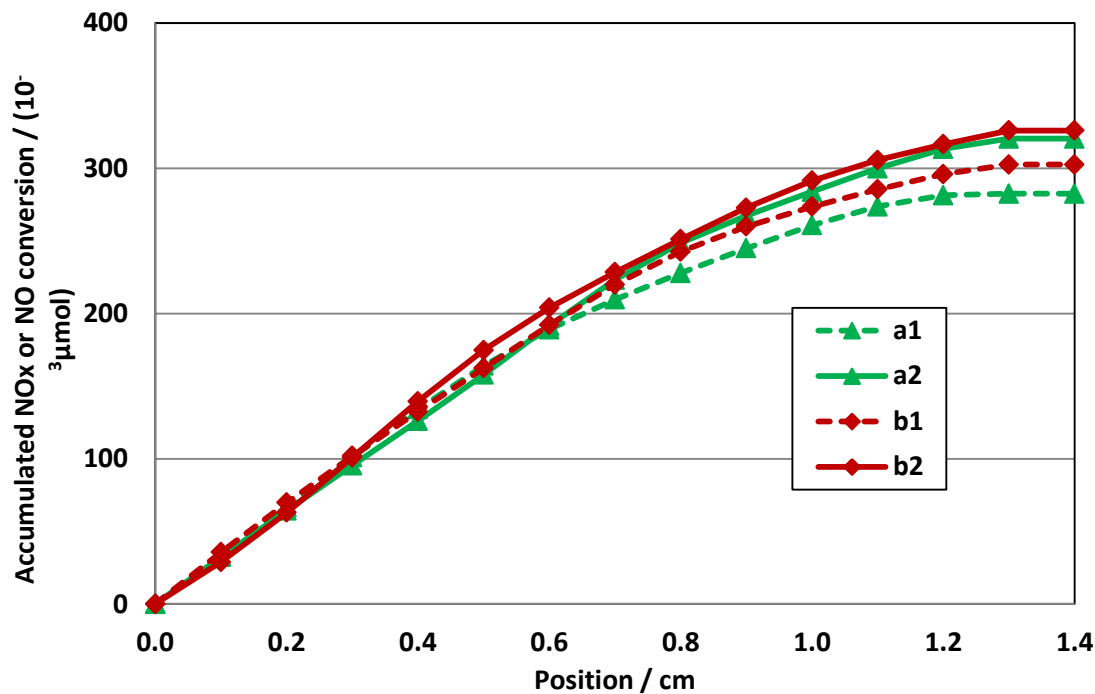


Figure 6.13(b). Effect of NH_3 storage on the standard and fast SCR reactions; conditions: 250°C; lightly aged catalyst; NH_3 inlet concentration: 419 ppm; 416 ppm; NO_x inlet concentration: 416 ppm; time gap between NH_3 pulsing adsorption and NO pulse: 10 seconds;
a1: 90 seconds NH_3 pulse adsorption followed by a 30 second NO_x (1:1 NO: NO_2) pulse;

- a2: 90 seconds NH_3 pulse adsorption followed by a 30 second NO pulse;
b1: 60 seconds NH_3 pulse adsorption followed by a 30 second NO_x (1:1 NO: NO_2) pulse;
b2: 60 seconds NH_3 pulse adsorption followed by a 30 second NO pulse.

6.4 Conclusions

NH_3 adsorption profiles along a Cu-zeolite SCR catalyst, standard and fast SCR reactions over a NH_3 -precovered SCR catalyst and NH_3 migration were investigated. When NH_3 pulse times were short, and the front part of the catalyst far from saturation, NH_3 adsorption profile shapes were similar. As the front part of the catalyst approached saturation, adsorption profiles of course leveled out in the front. It was found that when the catalyst was far from saturation, the NH_3 inlet concentration had a significant effect on NH_3 adsorption profile. For the same amount of input NH_3 , a high NH_3 inlet concentration with a shorter pulse time resulted in a steeper NH_3 adsorption profile. Catalyst aging and increasing adsorption temperature reduced the amount of NH_3 stored, resulting in flatter NH_3 adsorption profiles for the same NH_3 input level.

The NH_3 profiles changed after the pulse ended, demonstrating NH_3 migration. There were at least two kinds of adsorbed NH_3 : weakly adsorbed NH_3 and strongly adsorbed NH_3 , both of which react with NO or NO_x . Weakly adsorbed NH_3 desorbed and migrated within seconds, while strongly adsorbed NH_3 did not migrate significantly within the testing times used, at least at 250°C and 300°C. Aging had little effect on strongly adsorbed NH_3 , but did decrease the catalyst's ability to adsorb weakly bound NH_3 . Also, catalyst aging increased the migration phenomenon of weakly adsorbed NH_3 . The effect of temperature on NH_3 migration was similar to that of catalyst aging.

NH_3 adsorption profiles were compared with NO_x consumption profiles during the fast SCR reaction, run after the catalyst was exposed to NH_3 . NO_x consumption profiles were flatter than their corresponding NH_3 adsorption profiles due to NH_3 migration. The NO and NO_x consumption profiles during standard and fast SCR reactions on the catalyst pre-covered with NH_3 and having a similar NH_3 distribution were not different. Also, the effect of catalyst aging on the standard and fast SCR reactions after NH_3 exposure depended on the ratio of input quantities of NH_3 and NO or NO_x . With higher NH_3 coverage, the effect of aging was insignificant. When the NO and/or NO_x were greater than the available adsorbed NH_3 , the NO and/or NO_x consumption profiles indicate that the reaction was negatively affected. Similar to the effect of catalyst aging on SCR reactions, the effect of temperature on the standard SCR reaction on the catalyst pre-covered with NH_3 depended on the ratio of input quantities of NH_3 and NO, following the same trends.

Chapter 7 Conclusions and Recommendations for Future Work

7.1 Conclusions

1. Standard SCR, fast SCR and SCR with pure NO_2 can proceed at significantly different rates especially at 300°C or below, and can be correlated to the amount of catalyst used. The catalyst lengths used to achieve 80% conversion at 300°C were around 2.4, 1.2 and 0.5 cm, for the standard SCR, SCR with pure NO_2 and fast SCR reactions, respectively, under the conditions used.
2. Standard SCR performance on Fe/zeolites SCR catalyst is closely related to NO oxidation over active Fe sites. The reaction orders with respect to NO and O_2 are very close to 1 and 0.5 for both the standard SCR reaction and NO oxidation over the Fe zeolite catalyst tested (Appendix I). However, NH_3 has an inhibiting effect on the standard SCR reaction since it can competitively adsorb on the same active sites that participate in NO adsorption and oxidation. For standard SCR at 300°C or higher, the overall conversion was limited by insufficient NH_3 supply since part of the NH_3 is oxidized by O_2 and equimolar amounts of NH_3 and NO were added. Increasing the temperature past 300°C results in more significant NOx reduction since NO oxidation significantly increases, which also increases the selectivity of NH_3 reacting with NOx rather than O_2 .
3. NO_2 -SCR with equimolar NH_3 and NO_2 feed results in significant N_2O production, and N_2O formation tends to decrease with increasing temperature above 250°C . At temperatures between 300 to 400°C , besides the N_2O formation route, other reactions contribute to decreased N_2O formation, including the decomposition of NH_4NO_3 into HNO_3 then to NO_2 and O_2 , and/or NO_2 decomposition into NO and O_2 . At high temperatures, both the enhanced NO_2 -SCR to N_2 and N_2O decomposition at the back part of the catalyst contribute to decreased N_2O formation as well.
4. Different reaction patterns were observed for unbalanced NO: NO_2 ratios ($\neq 1$) at 300°C . At ratios larger than 1, the reaction proceeded in series, namely via fast SCR reaction first, followed by standard SCR. Otherwise, the reactions proceeded in parallel, with fast SCR and NO_2 -SCR occurring at the same time, beginning at the very front of the catalyst. The different patterns are determined by the relative reaction rates of the three types of SCR reaction.
5. Comparison between spatially-resolved test results and normal test results demonstrated that spatial resolution with FTIR is a reliable test technique. For the Cu-zeolite catalyst, our experiments suggest that the critical temperature at which the zeolite structure used experiences dramatic change lies between 700 and 800°C . For these tests, during hydrothermal aging in the tube reactor at 800°C , due to a radial temperature distribution in the reactor, heterogeneity in

aging occurred and hence resulted in activity distribution along the radial direction, but only for the highly aged sample.

6. Hydrothermal aging had little effect on NO oxidation activity. For standard SCR and fast SCR, NH_3 conversions changed monotonically with temperature and catalyst length. NH_3 overconsumption became significant when the reaction temperature was higher than 300°C , which limited the conversion of NO due to the lack of NH_3 . Therefore, for standard SCR and fast SCR, NO_x conversion attained its maximum at 300°C . In fast and standard SCR, hydrothermal aging decreased reaction rates for SCR and NH_3 overconsumption simultaneously. Selectivity to NH_3 overconsumption was higher over the highly aged catalyst at high temperatures, $>500^\circ\text{C}$. NO oxidation was observed at the outlet portion of the catalyst under standard SCR conditions at high temperatures, suggesting a balance between NO oxidation and SCR at limited NH_3 concentrations. NO conversion under standard SCR conditions was more heavily affected by hydrothermal aging than NO_x conversion for fast SCR. Correspondingly, NH_3 overconsumption was more significant under standard SCR conditions than that for fast SCR.
7. Fast SCR at high temperatures was limited by the decomposition of NO_2 at the front of the catalyst. Hydrothermal aging decreased the extent of NO_2 decomposition into NO at high temperatures, which helped maintain fast SCR reaction conditions in the catalyst. The effect of hydrothermal aging on NH_3 oxidation was more complicated. Generally, aging reduced NH_3 oxidation activity, but it did not change monotonically with aging extent; neither did the output of NO_x produced during NH_3 oxidation. However, the highly aged catalyst produced a higher proportion of NO_x . At 200°C , hydrothermal aging did not show appreciable effects on the SCR extent with various $\text{NO}:\text{NO}_2$ ratios.
8. NH_3 adsorption profiles along a Cu-zeolite SCR catalyst, standard and fast SCR reactions over a NH_3 -precovered SCR catalyst and NH_3 migration were investigated. When NH_3 pulse times were short, and the front part of the catalyst far from saturation, NH_3 adsorption profile shapes were similar. As the front part of the catalyst approached saturation, adsorption profiles of course leveled out in the front. It was found that when the catalyst was far from saturation, the NH_3 inlet concentration had a significant effect on the NH_3 adsorption profile. For the same amount of input NH_3 , a high NH_3 inlet concentration with a shorter pulse time resulted in a steeper NH_3 adsorption profile. Catalyst aging and increasing adsorption temperature reduced the amount of NH_3 stored, resulting in flatter NH_3 adsorption profiles for the same NH_3 input level.
9. The NH_3 profiles changed after the pulse ended, demonstrating NH_3 migration. There were at least two kinds of adsorbed NH_3 : weakly adsorbed NH_3 and strongly adsorbed NH_3 , both of which react with NO or NO_x . Weakly adsorbed NH_3 desorbed and migrated within seconds,

while strongly adsorbed NH_3 did not migrate significantly within the testing times used, at least at 250°C and 300°C. Aging had little effect on strongly adsorbed NH_3 , but did decrease the catalyst's ability to adsorb weakly bound NH_3 . Also, catalyst aging increased the migration phenomenon of weakly adsorbed NH_3 . The effect of temperature on NH_3 migration was similar to that of catalyst aging.

10. NH_3 adsorption profiles were compared with NO_x consumption profiles during the fast SCR reaction, run after the catalyst was exposed to NH_3 . NO_x consumption profiles were flatter than their corresponding NH_3 adsorption profiles due to NH_3 migration. The NO and NO_x consumption profiles during standard and fast SCR reactions on the catalyst pre-covered with NH_3 and having a similar NH_3 distribution were not different. Also, the effect of catalyst aging on the standard and fast SCR reactions after NH_3 exposure depended on the ratio of input quantities of NH_3 and NO or NO_x . With higher NH_3 coverage, the effect of aging was insignificant. When the NO and/or NO_x were greater than the available adsorbed NH_3 , the NO and/or NO_x consumption profiles indicate that the reaction was negatively affected. Similar to the effect of catalyst aging on SCR reactions, the effect of temperature on the standard SCR reaction on the catalyst pre-covered with NH_3 depended on the ratio of input quantities of NH_3 and NO , following the same trends.

7.2 Recommendations for Future Work

The application of the spatial resolution technique in the field of emission control catalysis for automobiles is critical. As long as there is inhomogeneous distribution of activity within the catalyst, spatial resolution can be used to investigate the formation of activity gradients. With such data, model validation and tuning is more readily accomplished. The obvious next steps would be to use the data obtained to build NH_3 adsorption and SCR reactivity models. Regarding NH_3 pulsing adsorption and the SCR reactions, it is recommended that an experimental study and model investigation be carried on simultaneously because there are many parameters not available at present. With the help of the model, the data obtained in the experiments can be used to verify the parameters obtained. For example, it is known that a Langmuir isotherm could not be used to describe NH_3 adsorption. It is quite possible that other established isotherms may not be able to describe the NH_3 adsorption and desorption process very well, because NH_3 adsorption is a complex phenomenon. It is quite evident that there are at least two types of adsorption sites in the process. Experiments are needed to decide parameters for those two types of adsorption and desorption. In the meantime, when surface reactions are considered in the system, the reaction parameters for the reactions between NO_x and differently adsorbed NH_3 shall be decided by experiments too.

Another application of spatial resolution technique is in the field of catalyst degradation. As degradation is typically not homogeneous, spatial resolution can be used to characterize sulfur poisoning for example, and demonstrate what portions of the catalyst and what reactions are affected by sulfur exposure.

Appendix I SCR Catalyst Performance Tests – Outlet Measurements

AI. 1 Introduction

In this section, data are presented from experiments that were run to verify that the reactor system is inert. Following this, experiments were run to verify catalyst performance, including NH_3 adsorption and temperature programmed desorption (TPD), NH_3 oxidation, NO oxidation, standard SCR and fast SCR. Also the effects of propylene on the standard and fast SCR reactions were investigated.

The experiment set up was the same as that described in Chapter 3. Two samples of catalysts were tested, Fe-zeolite and Cu-CHA, provided by General Motors Global R&D.

AI. 2 Results and discussion

AI.2.1 Reactor effects

The purpose of this set of experiments was to verify that the reactor system is inert. Based on planned experiments, the reactor should not impact any reactions at temperatures as high as 500°C in the quartz tube. Preliminary results showed that the upstream and downstream tubing temperatures were critical. However, the upstream tubing temperature must be high enough to avoid water condensation and the downstream hot enough to avoid condensation and NH_3 hold-up. At the same time, the upstream and downstream tubing temperature should not be too high, in order to avoid reaction.

Three experiments were conducted. They were NH_3 oxidation, standard SCR, and transient experiments with changing NO and NH_3 concentrations and NO_2 to NO ratios, all from 100 to 500°C .

With the upstream tubing temperature set at 180°C , there was no evidence of reaction. However, it was found that standard stainless steel tubing downstream of the reactor caused significant extents of NH_3 oxidation and SCR reaction. In an attempt to eliminate any reaction, a test with the outlet tubing coated with an advertised inert material, produced by Restek and called Silconert, was evaluated. In SCR tests with the coated tubing, when the temperature in the reactor was 500°C , the outlet tubing reached 132°C , and there was no NH_3 consumed. When the downstream tubing temperature was 142°C , via providing extra heating, some conversion was noted but only with low H_2O levels.

AI.2.2 NH_3 adsorption and temperature programmed desorption

A key step in the reaction sequence is NH_3 adsorption on the catalyst. Therefore, the catalyst's NH_3 storage capacity is critical to overall performance. In this experiment, the catalyst's NH_3 adsorption capacity was measured and NH_3 desorption profiles as a function of temperature evaluated.

The space velocity was $15,000 \text{ hr}^{-1}$ (STP) and the inlet concentration of NH_3 was around 310 ppm. First, the catalyst was cleaned with 8% O_2 , 5% H_2O , 5% CO_2 and a balance of N_2 at 500°C for 15 minutes. After cooling the reactor to 155°C , NH_3 was introduced into the system with 5% H_2O , 5% CO_2 and a balance of N_2 . When the outlet NH_3 concentration was equal to the inlet concentration, the catalyst was considered

saturated. The NH_3 was then switched off, the system allowed to re-achieve steady-state and then the reactor heated to 500°C .

The adsorption time was approximately 15 minutes when testing the Fe-zeolite catalyst. The adsorption and desorption profiles are shown in Figure AI.1(a). At 155°C , $83.8 \pm 3.9 \mu\text{mol NH}_3$ per gram of catalyst adsorbed. During the temperature programmed desorption (TPD), $86.3 \pm 11.6 \mu\text{mol NH}_3$ per gram of catalyst desorbed. The data obtained when testing the Cu-zeolite catalyst are shown in Figure AI.1(b). The amount that adsorbed was $117 \pm 5.5 \mu\text{mol/gram}$ and $111 \pm 14.9 \mu\text{mol/gram}$ desorbed. The relatively large measurement error was due to the long-time scales involved in the experiment. Compared to the measurement errors, the difference between adsorption and desorption quantities was not significant. The peak in NH_3 desorption for Fe-zeolite occurred at 306°C and for Cu-zeolite at 225°C . The peak desorption temperature is a function of the bonding strength between adsorbent and adsorbate. The data indicate that NH_3 can be adsorbed more strongly on Fe-zeolite. Comparing the desorption profiles of these two catalysts, it is obvious that there are multiple desorption peaks for Cu-zeolite, indicating multiple NH_3 adsorption sites exist, which is in line with previously published results [106].

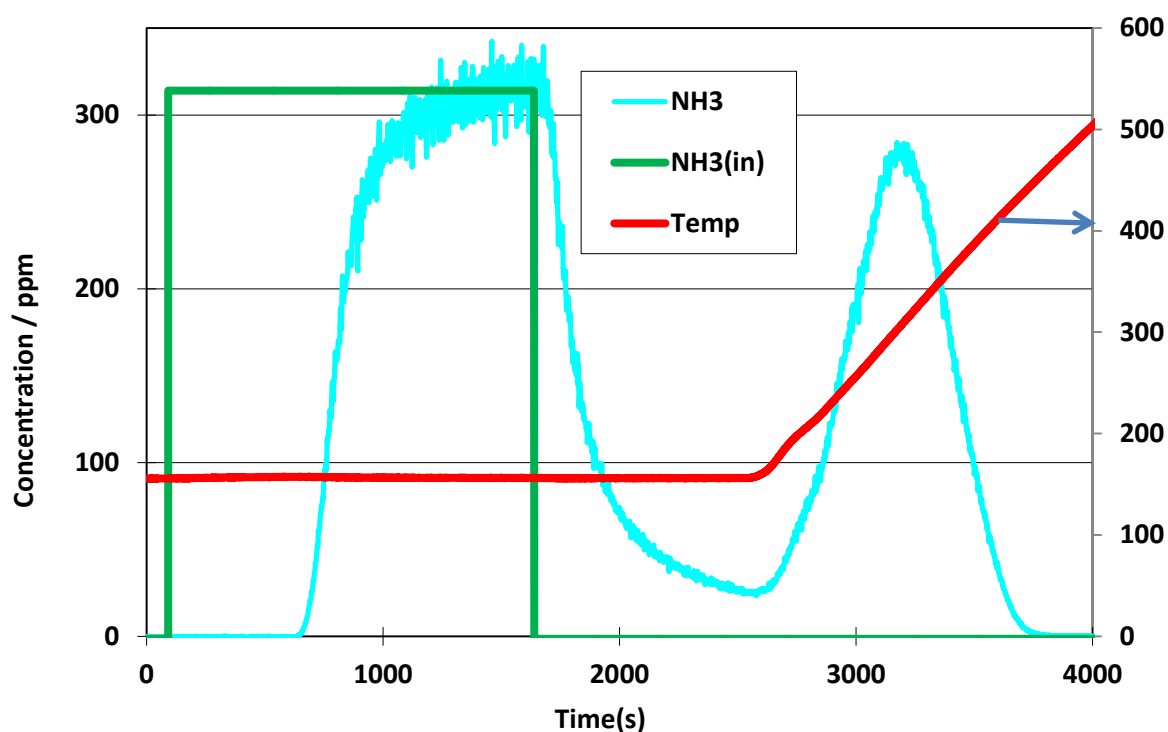


Figure AI.1(a) NH_3 adsorption and desorption profile (Fe-zeolite)

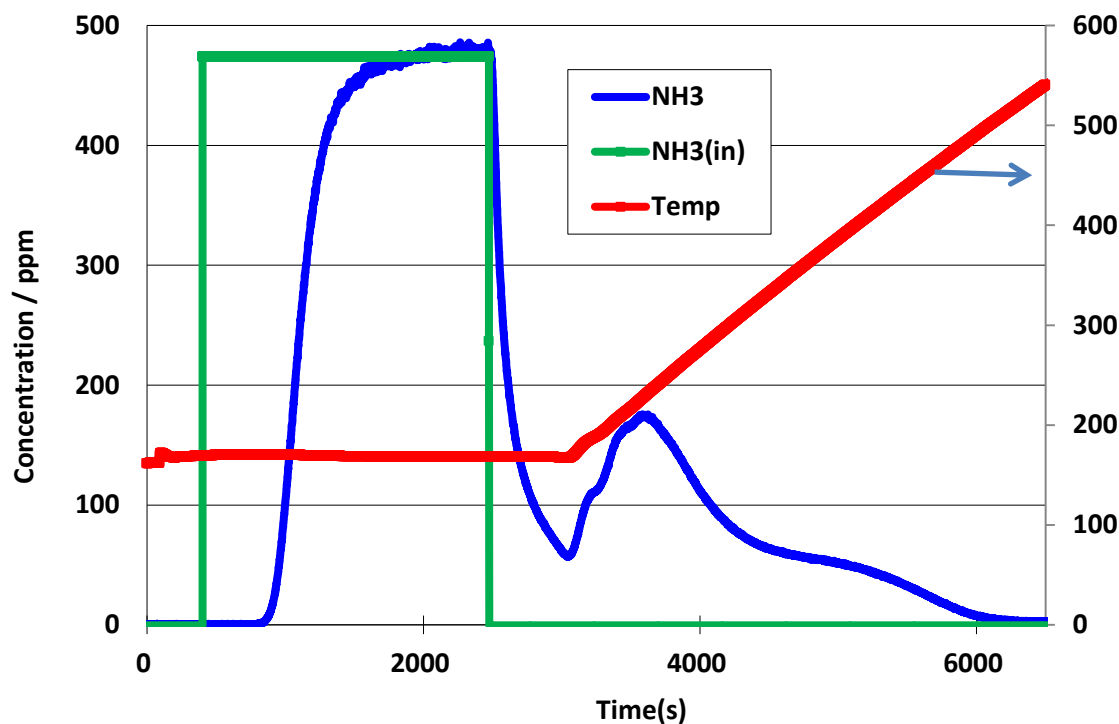


Figure AI.1(b) NH_3 adsorption and desorption profile (Cu-zeolite)

AI.2.3 NH_3 oxidation

NH_3 oxidation by O_2 is an unwanted side reaction, as it consumes the NH_3 reactant that would otherwise be used in the SCR reaction. The effects of temperature, and inlet NH_3 , O_2 and water concentrations on NH_3 oxidation were evaluated.

Again, both catalyst sample types were tested. The space velocity for these experiments was $28,000 \text{ hr}^{-1}$. The concentrations of NH_3 , O_2 and H_2O were varied. Data were collected when steady state was reached. As shown in Figure AI.2(a), with the Fe-based catalyst, increasing the amount of inlet NH_3 led to lower overall conversions. The onset of a “light-off” was observed above 350°C , indicating that only at higher temperatures would NH_3 oxidation be a concern. Data obtained when using the Cu-zeolite catalyst are shown in Figure AI.2(b), and show the same trends to different extents. Again, higher levels of NH_3 led to less oxidation, but the “light off” temperature was less than 350°C and extent of oxidation was higher over the Cu catalyst, reaching 100% conversion by 500°C .

O_2 concentration had little effect on the conversion at low temperature, as shown in Figure AI.3 for Fe-zeolite. At higher temperature the effect became more significant, with increasing O_2 concentration leading to increased NH_3 oxidation. The effect of H_2O concentration was also evaluated, with results also shown in Figure AI.3 for Fe-zeolite. Increasing H_2O levels resulted in decreased NH_3 oxidation, although the changes were slight. Data obtained when using the Cu-zeolite catalyst show the same trends to

different extents regarding the effect of initial NH_3 concentration, water content and oxygen concentration. Again, higher levels of NH_3 led to less oxidation, but the extent of oxidation was higher over the Cu catalyst, reaching 100% conversions by 500°C.

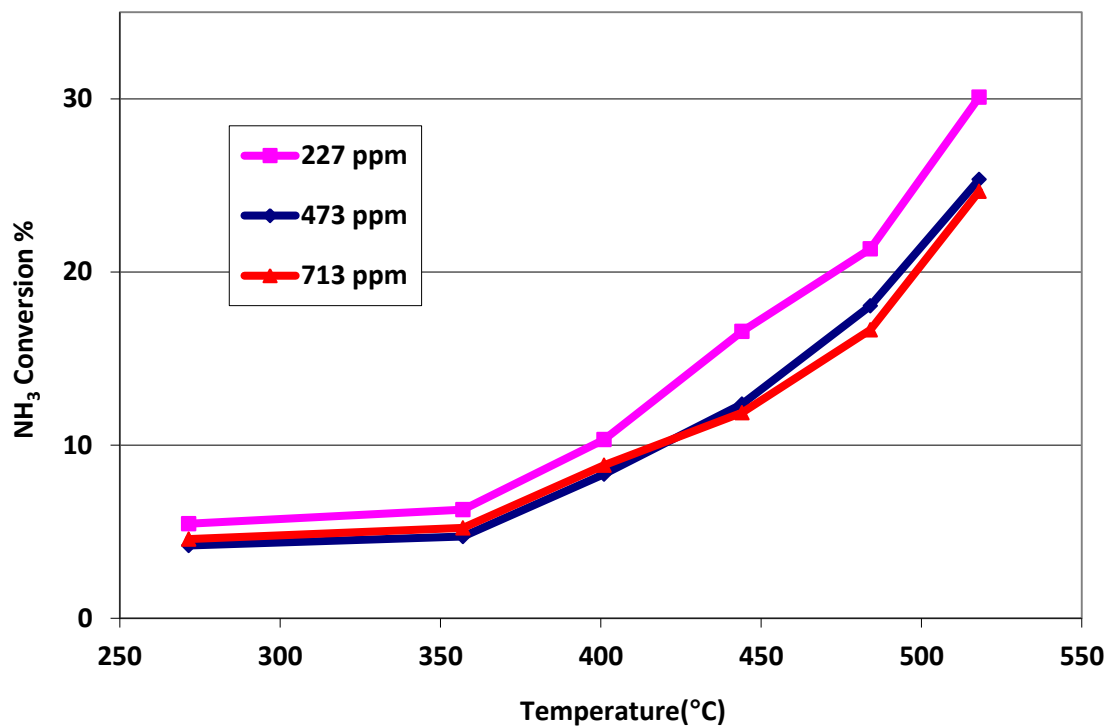


Figure A1.2(a) Effect of NH_3 concentration on NH_3 oxidation (Fe-zeolite)

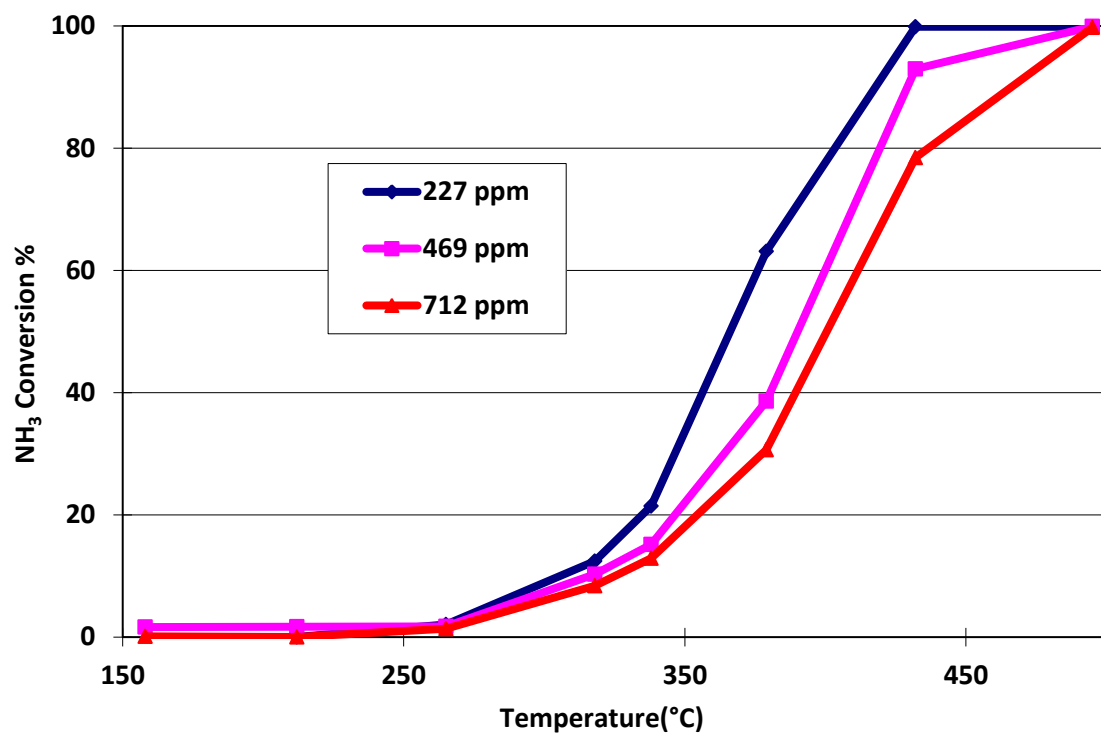


Figure A1.2(b) Effect of NH₃ concentration on NH₃ oxidation (Cu-zeolite)

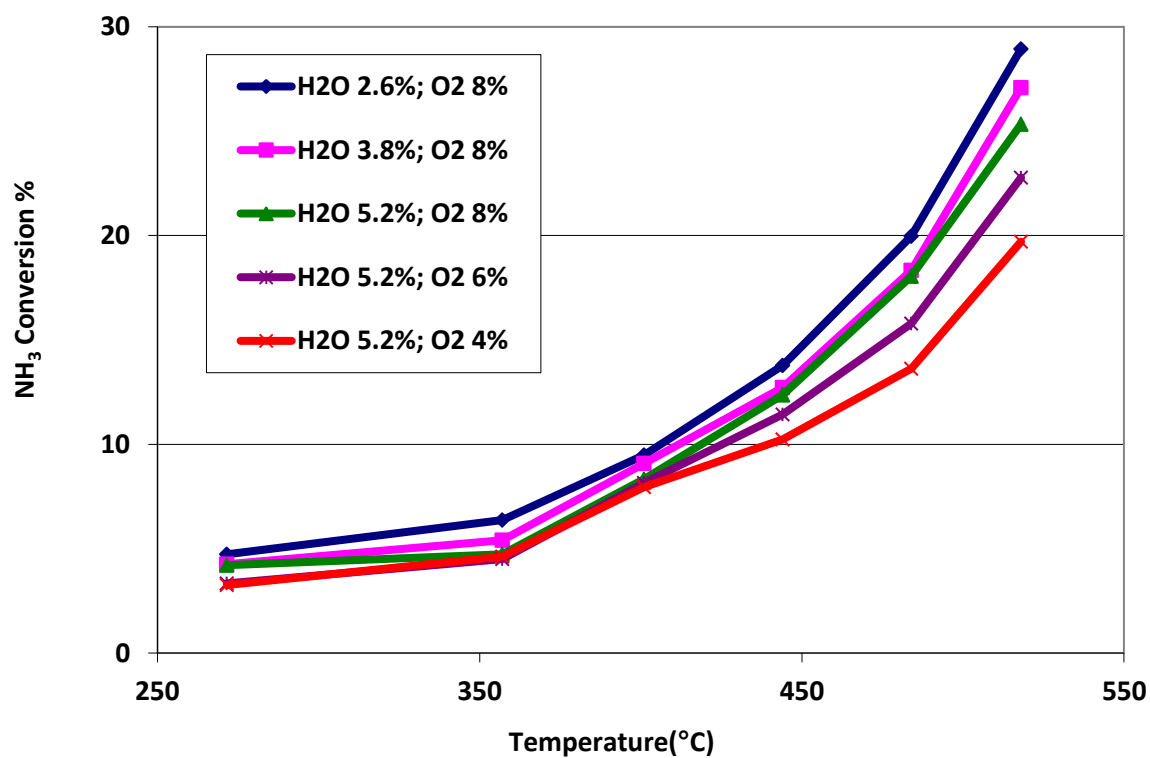


Figure AI.3 Effect of O₂ and H₂O concentrations on NH₃ oxidation (Fe-zeolite)

AI.2.4 NO oxidation

As mentioned in Chapter 2, there are the standard and fast SCR reactions, with the latter depending on a 1:1 ratio of NO and NO₂. As most NOX exiting an engine is NO, the catalyst's ability to oxidize NO is important in driving the fast reaction. The effect of temperature, and inlet NO, O₂ and water concentrations on the conversion of NO to NO₂ were studied. Both catalysts were tested for NO oxidation. The catalysts and test conditions were the same as that in NH₃ adsorption experiment. The concentrations of NO, O₂ and water were changed. Data were collected after steady-state had been reached.

The effect of inlet NO concentration is shown in Figure AI.4 and the effects of H₂O and O₂ are shown in Figure AI.5, for the Fe-based catalyst. For all cases, NO oxidation conversion increased until about 425°C, and then decreased. The decrease at high temperature is due to thermodynamic limitation, with the reaction kinetically limited at the lower temperatures. NO conversion decreased as the inlet concentration increased. As shown in Figure AI.5, NO conversion increased with increasing O₂ content, and decreased with increasing water, which is in agreement with published observations [93, 169, 193]. According to the explanation given by Metkar et al, the negative effect of water on NO oxidation might be due to the reaction between H₂O and product NO₂, which could form a mixture of HNO₂ and HNO₃. Those two products would likely remain adsorbed on the active sites required for the NO oxidation reaction [93].

Tests with the Cu-zeolite demonstrated that it was less effective for NO oxidation, with the data shown in Figure AI.6. As with the Fe sample, conversion increased until about 460°C, which in this case was the maximum temperature tested. Higher temperatures would have ultimately led to thermodynamic limitation. The effect of inlet NO concentration on conversion is similar to that of the Fe system. Also, the effects of water and O₂ on NO to NO₂ conversion were similar to that of the Fe system.

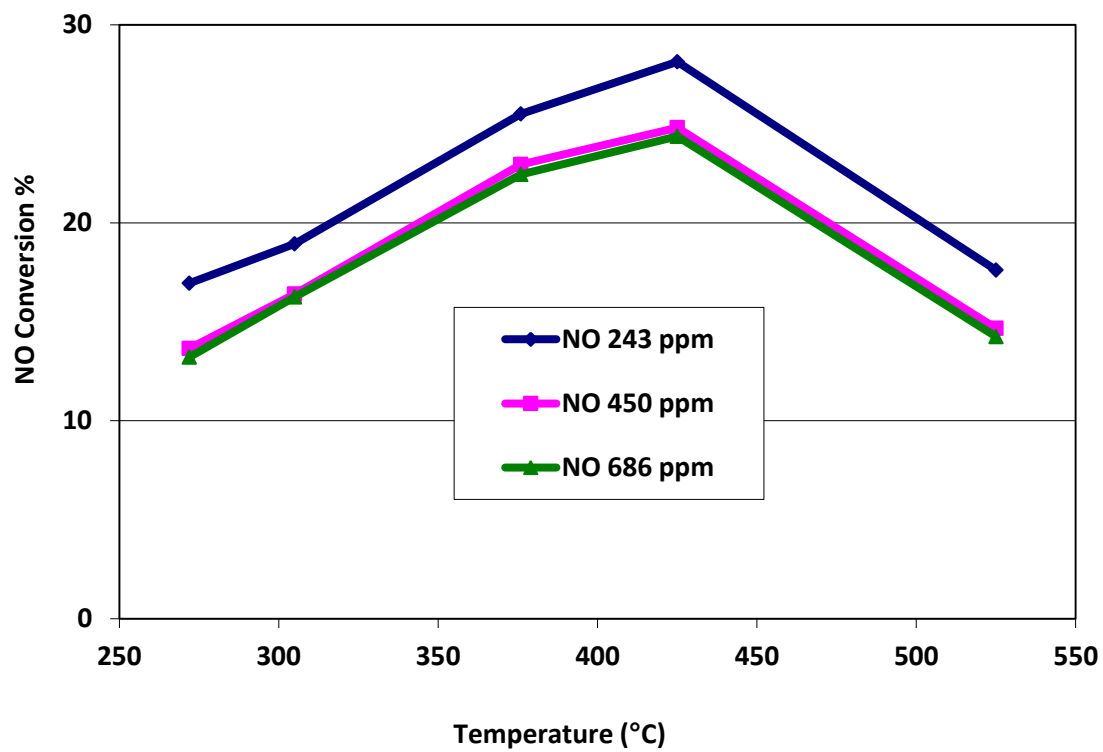


Figure AI.4 Effect of NO concentration and temperature on NO to NO₂ conversion (Fe-zeolite)

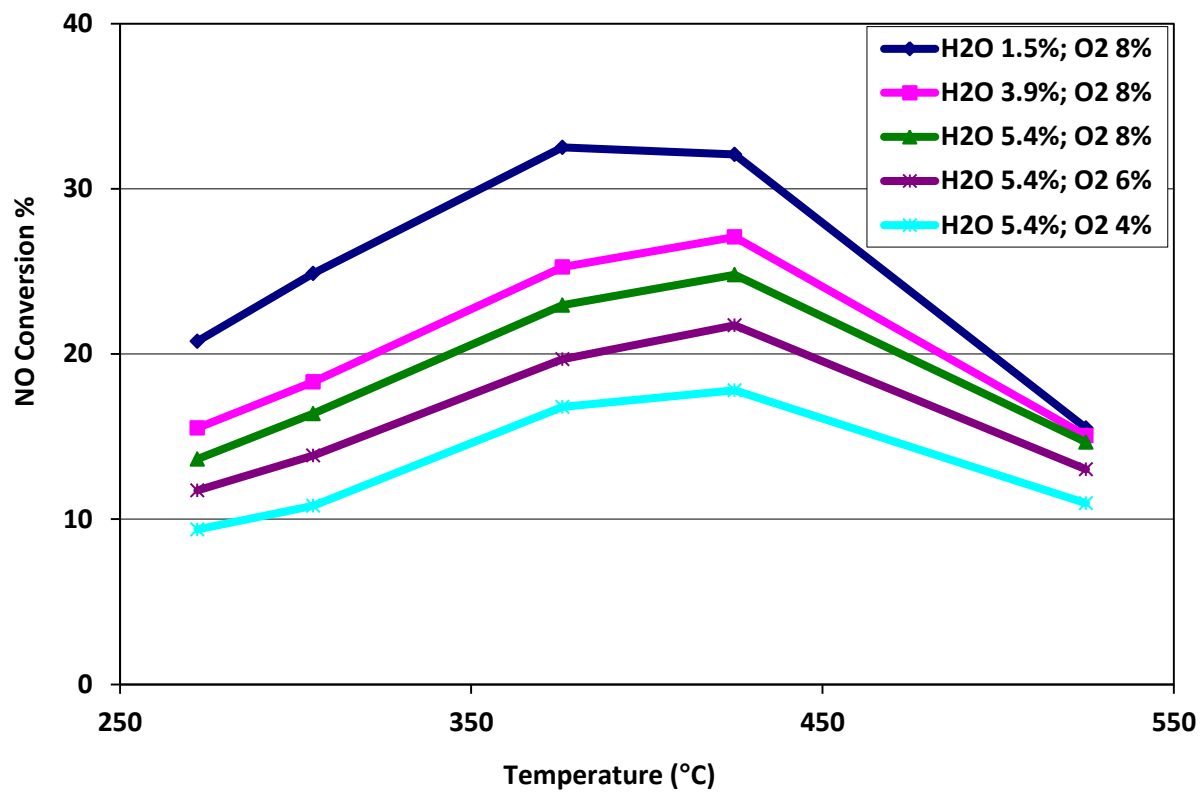


Figure A1.5 Effect of H₂O and O₂ content on NO to NO₂ conversion (Fe-zeolite)

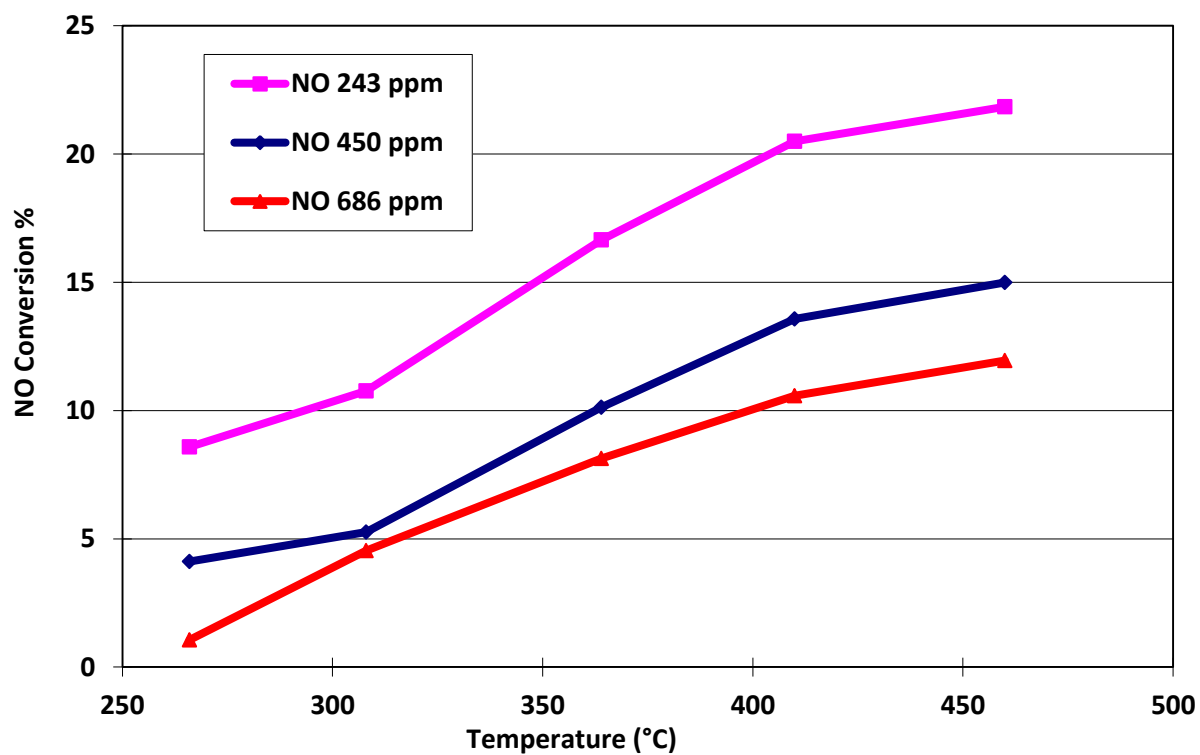


Figure AI.6 Effect of NO concentration and temperature on NO to NO₂ conversion (Cu-zeolite)

AI.2.5 SCR with NO only

The objective of these experiments was to evaluate common factors, such as temperature, inlet NO and NH₃ concentrations, as well as water and O₂ content on the NO conversion. With NO only as the inlet NO_x species, this is a characterization of the standard SCR reaction.

The inlet concentrations of NO, NH₃, O₂, and water were varied. Each experiment was conducted at a set inlet temperature and every experiment was run for enough time so that steady-state was reached. The space velocity was 28,000 hr⁻¹ for all the experiments.

NO conversions as a function of inlet NH₃ and NO concentrations over the Fe-zeolite catalyst are shown in Figures 4.7 and 4.8. NO conversion was affected by inlet NH₃ and NO concentrations and temperature. The NH₃ and NO concentration effects are related to NO:NH₃ ratios. When the NO:NH₃ ratio is larger than 1, there is not enough NH₃ to reduce NO. NO conversion is limited by NH₃ quantity. When the NO:NH₃ ratio is less than 1, NO conversion could be higher. However, NO conversion is also affected by temperature because the quantity of NH₃ available for NO reduction depends on how much NH₃ is consumed by O₂, which increases with temperature. NO conversion increased as temperature increased, when there is enough NH₃ available for NO reduction. When the NH₃ concentration was higher than that of NO, the NO conversion reached 100%, at around 350°C, which is in line with previous studies [106].

The effects of inlet O₂ and water concentrations on NO conversion are shown in Figure AI.9. The conversion of NO increases as the concentration of O₂ increases when the temperature was less than 300°C, indicating that the reaction order for O₂ is positive, in line with other reports [7, 35]. The effect of water on the conversion of NO and NH₃ in the system was not significant.

The effects of inlet NO and NH₃ concentrations and temperature on the performance of a Cu-zeolite system were also studied and similar trends observed. One difference is that the NH₃ was completely consumed at temperatures above 500°C, due to SCR and NH₃ oxidation. This leads to lower NO conversions at intermediate temperatures, although complete conversions were obtained at 500°C, when sufficient NH₃ was added. A significant amount of N₂O was also produced as the NO/NH₃ conversion increased. According to the mechanism proposed by Krieg et al [73], for the case of Cu-zeolite, N₂O is produced due to the presence of CuO. As a byproduct, the production of N₂O increases with the conversion of NO/NH₃. Similar to the Fe system, O₂ had a slight positive effect on conversion, while H₂O showed little effect.

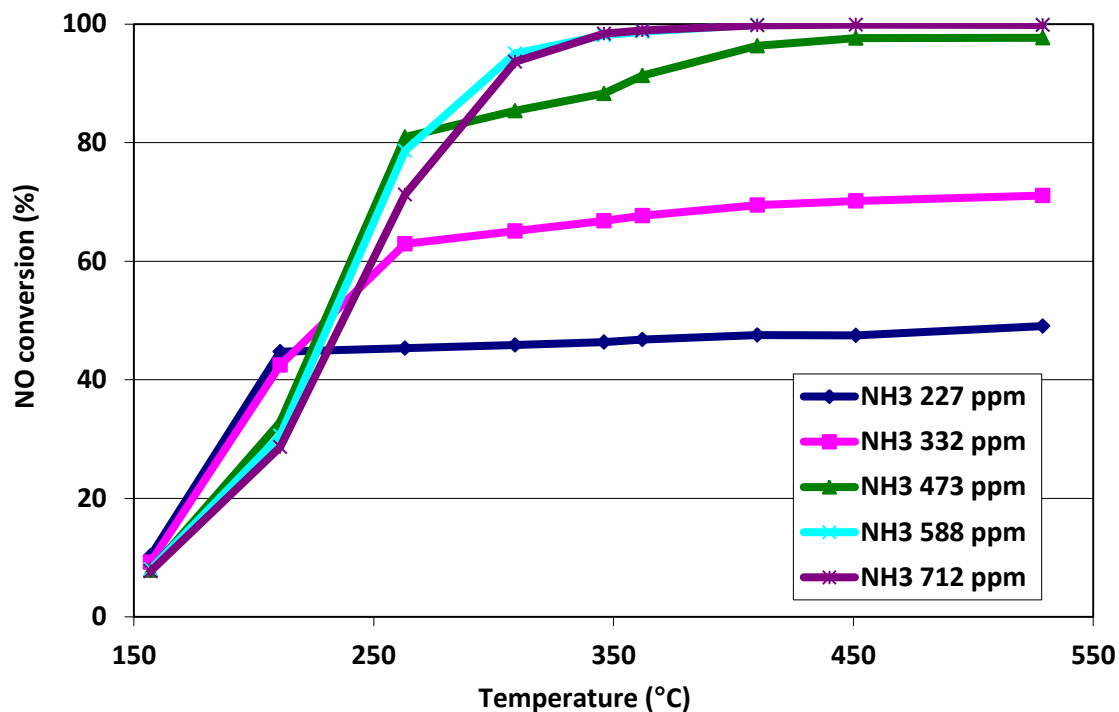


Figure AI.7(a) Effect of temperature and NH_3 concentration on NO conversion
(Fe-zeolite, NO concentration fixed at 450 ppm)

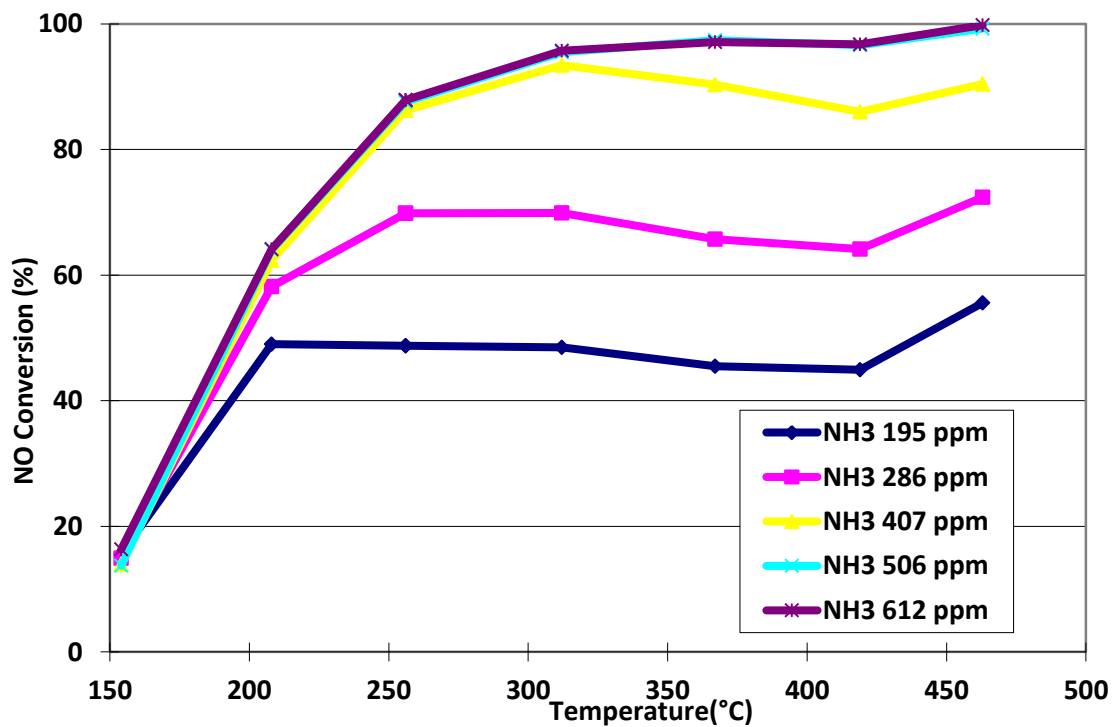


Figure AI.7(b) Effect of temperature and NH_3 concentration on NO conversion
(Cu-zeolite, NO concentration fixed at 450 ppm)

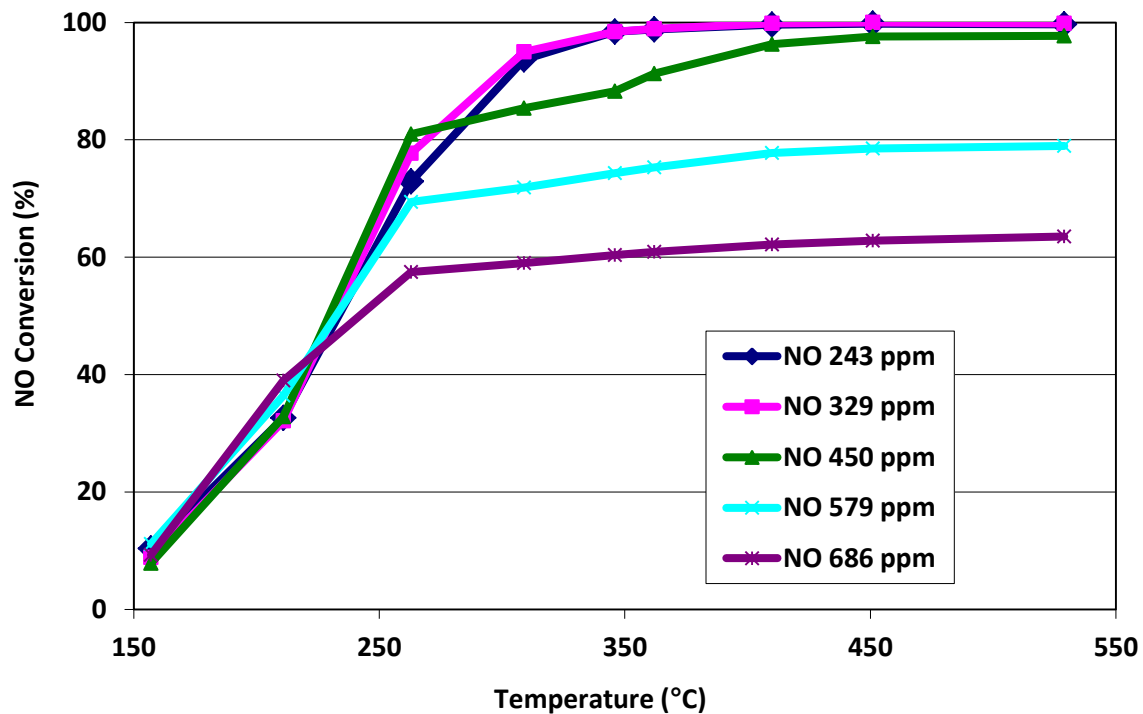


Figure A1.8 Effect of temperature and NO concentration on NO conversion
(Fe-zeolite, NH₃ concentration fixed at 473 ppm)

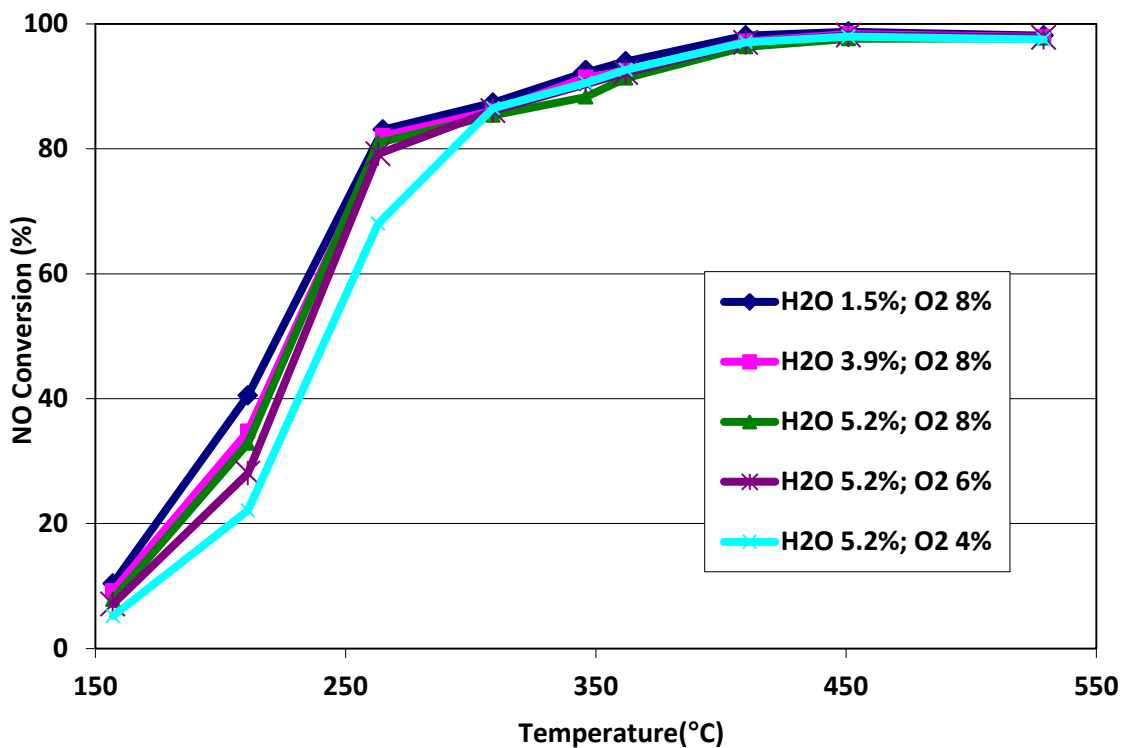


Figure AI.9 Effect of O₂ and H₂O content on NO conversion

(Fe-zeolite, NH₃ = 473 ppm; NO = 450ppm)

AI.2.6 SCR with NO and NO₂

The objectives of these experiments were to evaluate the effect of NH₃ concentration on the conversion of NH₃ and NO_x, and investigate the effect of NO:NO₂ ratio on the conversion of NO_x and the production of N₂O. The ratio of NO:NO₂, and inlet NH₃, O₂, and water concentrations were varied. Data were obtained once steady-state had been reached. The space velocity was the same for all the experiments, 28000 hr⁻¹.

The effect of the inlet NH₃ concentration and temperature on the conversion of NO_x in the NO:NO₂ system was similar to that for the standard SCR reactions. The effect of NO:NO₂ ratio on NO_x conversion is shown in Figure AI.10. When the ratio of NO:NO₂ is around 0.7 to 1.0, the conversion of NO_x reached the maximum. As the NO:NO₂ ratio increased beyond that, the NO_x conversion decreased, especially at low temperature.

When the ratio of NO:NO₂ was close to 1, the fast SCR reaction is likely dominant, thus the NO_x conversion reached its maximum. When the ratio of NO:NO₂ is less or larger than 1, some fast SCR occurs, but so do the standard reaction and the reaction between NO₂ and NH₃, which are relatively slower. At low temperature, the standard reaction is more kinetically limited than the fast reaction, and therefore, changing the NO:NO₂ is more significant. At higher temperatures, both reactions are kinetically fast and the effect of NO:NO₂ ratio on SCR reaction is not so outstanding.

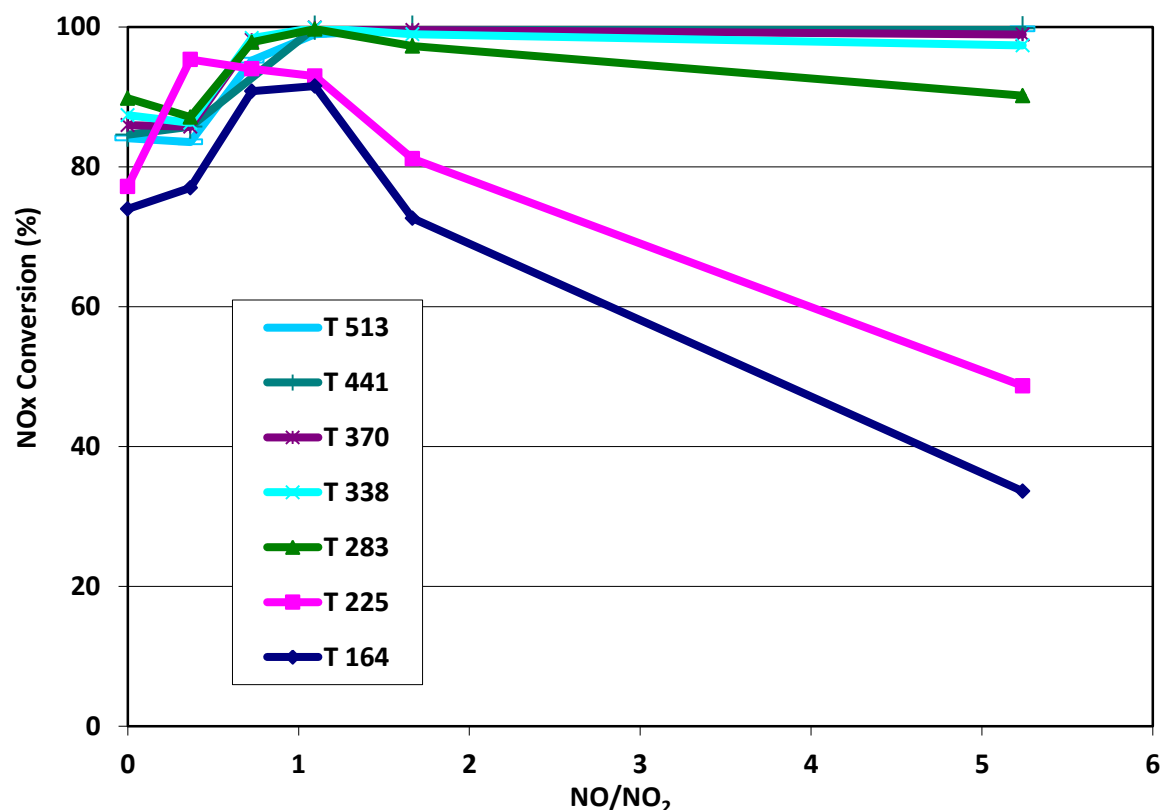


Figure AI.10 Effect of NO:NO₂ ratio on NO_x conversion (Fe-zeolite)

AI. 3 Conclusions

The reactor system was verified to be inert for SCR reactions when the outlet tubing was coated with an inert material called Silconert.

NH₃ adsorption and temperature programmed desorption were done on Fe- and Cu-zeolite catalysts at 155°C. For Fe-zeolite, 83.8±8.3 μmol of NH₃ was adsorbed per gram of catalyst. The peak in NH₃ desorption occurred at 306°C. For Cu-zeolite, 117±11 μmol of NH₃ was adsorbed per gram of catalyst. The peak in NH₃ desorption occurred at 225°C. The higher peak desorption temperature for Fe-zeolite indicated that the bonding between NH₃ and Fe-zeolite is stronger than that between NH₃ and Cu-zeolite. The effects of NH₃, H₂O, and O₂ inlet concentrations on NH₃ oxidation were investigated on both Fe- and Cu-zeolite catalysts. On the Fe-zeolite catalyst, the onset of a light-off was observed above 350°C. Higher levels of NH₃ concentration led to less oxidation, indicating that NH₃ might be inhibiting NH₃ oxidation on Fe-zeolite. However, increasing O₂ concentration led to increased NH₃ oxidation. Data obtained when using the Cu-zeolite catalyst show the same trends to different extents, but the extent of oxidation was higher over the Cu catalyst.

The effect of NO, H₂O, and O₂ inlet concentrations on NO oxidation were investigated on both Fe- and Cu-zeolite catalysts. On the Fe-zeolite catalyst, NO oxidation conversion increased until about 425°C and

then decreased. NO conversion decreased as the inlet concentration increased. NO conversion increased with increasing O₂ content, and decreased with increasing water content. Similar trends were found for Cu-zeolite regarding the effect of NO, H₂O and O₂ inlet concentrations.

In the standard SCR reaction, NO conversion is a function of inlet NH₃ and NO concentration, as well as temperature. Over the Fe-zeolite catalyst, NH₃ and NO concentration effects are related to NO:NH₃ ratios. NO conversion increased with temperature. When the NH₃ concentration was higher than that of NO, the NO conversion reached 100% at around 350°C. The conversion of NO increased with O₂ inlet content when the temperature was lower than 300°C. Similar trends were observed over the Cu-zeolite catalyst. However, the oxidation of NH₃ was more extensive over the Cu catalyst. A significant amount of N₂O was also produced as the NO/NH₃ conversion increased.

The effect of NO:NO₂ ratio on NO_x conversion was examined. When the ratio of NO:NO₂ was around 0.7 to 1.0, the NO_x conversion reached the maximum. At low temperature, the standard reaction is more kinetically limited than the fast reaction. Therefore, changing the NO:NO₂ was more significant. At higher temperatures, both reactions are kinetically fast and the NO:NO₂ ratio had less effect.

Appendix II Sampling Amount Determination for NH₃ Pulsing Adsorption

The presence of the capillary could affect the flow pattern in the channel. In order to keep the experimental data relevant or the interpretation as accurate/quantifiable as possible, the volumetric flow rates should be kept consistent while the capillary was being positioned at different points along the channel. To do that, the sum of the volume flow rate through the capillary and that through the annular space between the capillary and the channel should be kept the same during the process of sampling. In other words, when the flow rate thorough the annular space is reduced, the flow rate though the capillary should be correspondingly increased.

The software COMSOL[®] has been used to simulate the flow of gases through the capillary and the annular space between the wall of the channel and capillary. The calculation procedure can be broken down into three steps.

The first step is to evaluate the pressure in front of the channel. As the total flow rate through the reactor was known, the flow rate through each channel can be calculated by dividing the total volumetric flow rate by the number of channels. The outlet pressure of the reactor can be monitored; therefore, the pressure in front of the channel can be estimated with a COMSOL simulation, assuming the temperature is isothermal around the catalyst.

The second step of the calculation is to evaluate the volumetric flow rates through the annular space when the capillary is located at different points along the channel. From the first step of the calculation, the pressures in the front and the rear of the catalyst are known. The flow rate through the annular space can be determined, assuming the capillary is positioned in the radial center of the catalyst channel. Consequently, with the knowledge of the flow rate though the annular space, the volumetric flow rate through the capillary could be determined.

The final step of the calculation is to check whether the sampling process has significant effect on the flow rate through the annular space. The results indicate that when the gases were sampled, the flow rates though the annular space were not significantly affected in the front part of the catalyst, which means that this sampling method could keep the flow rates through the channel the same when the capillary was positioned at various points along the channel.

The structure of the catalyst channel and capillary is shown in Figure A1-1. The cross section of the channel is a square, of which the outer length is 1.47 mm. The thickness of the wash coat along the wall is 0.05 mm. The outer and inner diameters of the capillary are 0.68 mm and 0.57 mm, respectively. It is assumed that capillary is positioned in the radial center of the channel. For the gas phase, gravity has very little effect on the flow; therefore gravity was not considered in the modeling. With these assumptions, the

system can be considered as symmetric. To reduce the amount of calculation, the calculation can be conducted in a quarter of the system, as shown in Figure A1-2.

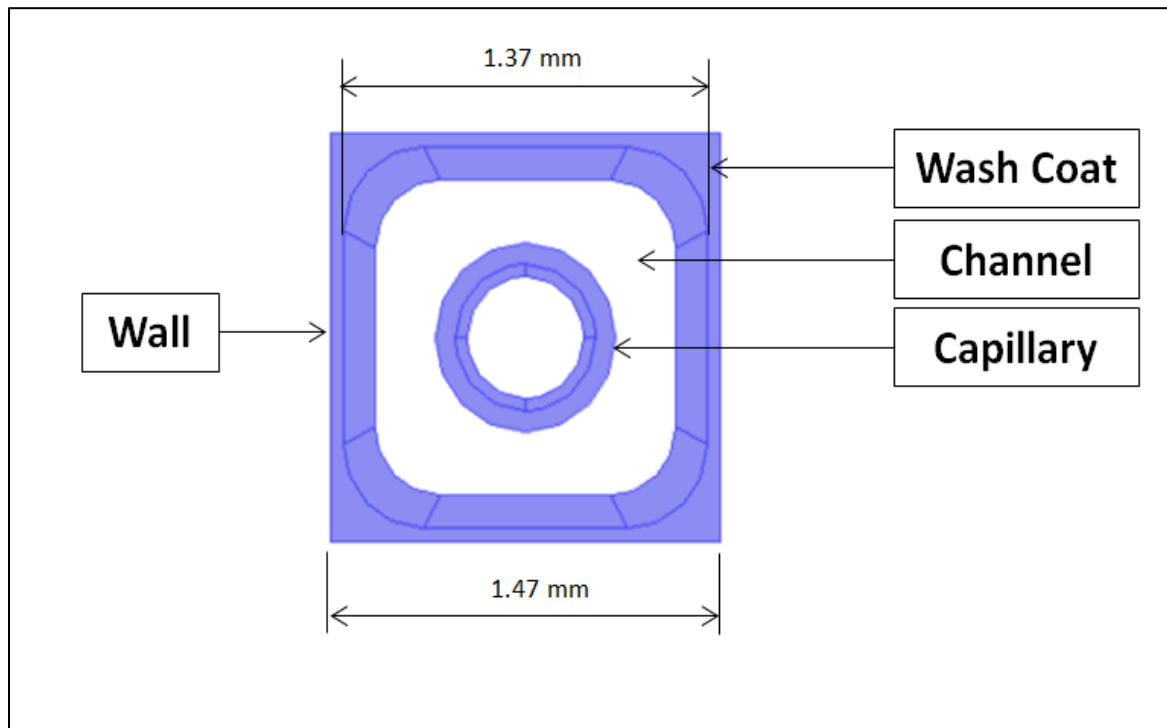


Figure AII-1 Structure of the catalyst channel and capillary

The total volume flow rate through the reactor was 3 L/min at standard temperature and pressure. There were 105 cells in the monolith catalyst. The area of the cross section of the free space in the channel when there is no capillary is $1.858 \times 10^{-6} \text{ m}^2$. It was assumed that there was no temperature distribution within the catalytic reactor and the temperature is 523K for this check. The velocity through an empty cell will be 0.4911 m/s. The pressure at the back of the catalyst is $1.2532 \times 10^5 \text{ Pa}$, based on the experiment data obtained. The Reynolds number for the flow through the channel is less than 2000, therefore, it was considered laminar. A laminar flow model in COMSOL was chosen to estimate the pressure at the front of the catalyst channel.

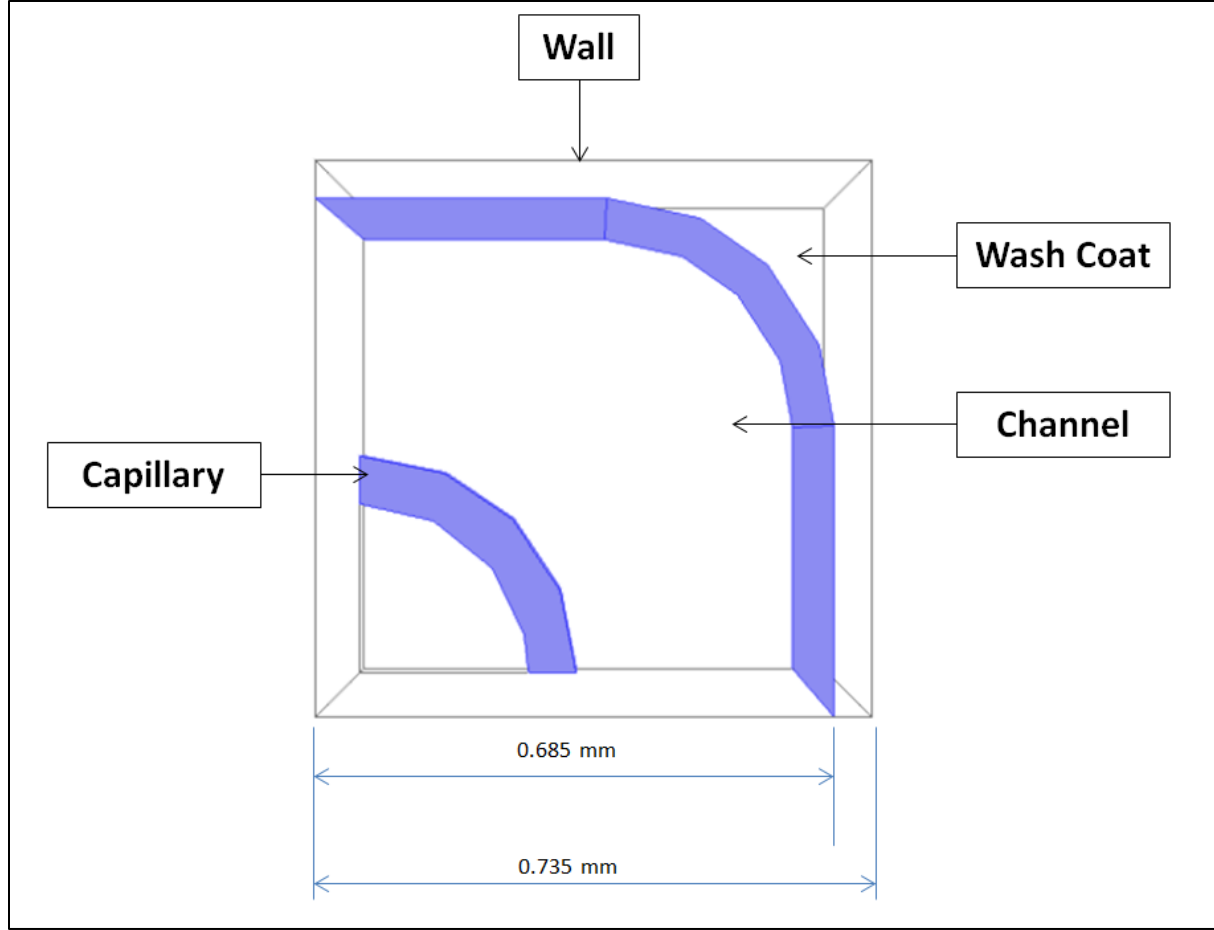


Figure AII-2 A quarter of the structure of the catalyst channel and capillary

The governing equations are as follows.

For the conservation of momentum,

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p \mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu(\nabla \cdot \mathbf{u}) \mathbf{I}] + \mathbf{F} \quad (\text{AII.1})$$

Where $F = 0$ since gravity was not considered. As the main contents of the gas were N_2 , O_2 and CO_2 , the gas properties, such as density and viscosity, can be represented by those of air.

For the conservation of mass,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (\text{AII.2})$$

where ρ is the density of air at 523K,

μ is the viscosity of air at 523K,

p is pressure

$\mathbf{I}$ is unit vector

T means vector transpose operation.

The boundary conditions are as follows.

The inlet velocity is $u = 0.4911 \text{ m/s}$, and the pressure at the outlet is $1.2532 \times 10^5 \text{ Pa}$.

The pressure at the front of the catalyst channel was calculated to be $1.2533 \times 10^5 \text{ Pa}$.

With the inlet pressure being known, the volume flow rate through the annular space between capillary and wash coat could be estimated. Volumetric flow rates through the annular space, for ten capillary positions, were estimated at 523K, with data shown in Table AII-1. Figure AII-3(a) and (b) shows how the capillary was positioned in the channel for two cases. The volumetric flow rate through the annular space depends on how much of the channel is occupied by the capillary. The relationship is shown in Figure AII-4. The data show that when the capillary is moved back through the catalyst channel, the flow through the annular space increases non-linearly, following a 3rd order polynomial trend.

To keep the total volumetric flow rate through the channel the same, the amount of sampled gases through the capillary needs to be changed based on the volumetric flow rate through the annular space. In Table AII-1, Column F shows the volumetric flow rates through the capillary when the capillary was positioned at different points. Those are the values against which the experimental data shall be compared. The last step of the calculation is to check how significant the effect that the sampling process could be on the flow rate through the annular space. In this calculation, velocity at the end of the capillary is set as a boundary condition, in addition to the pressure conditions for the front and rear of the catalyst channel. The volumetric flow rates through the annular space were calculated, with data shown in Column I in Table AII-1. The effect of sampling on the flow rates through the annular space is shown in Column J, and indicates that this sampling method has minimal effect on the flow rate through the annular space, which means that the total flow through the channel is approximately constant when capillary was positioned at differently along the channel.

The calculation of the values from Column A to J is shown as follows.

$$B = 2.0 - A$$

Values in Column C are obtained from modeling. As there are four sections of the annular space in reality, values in Column D are calculated as,

$$D = C * 60 * 4$$

Considering the effect of temperature on volume flow rate, values in Column E can be calculated as,

$$E = D * 273 / 523$$

The total volume flow rate through the channel is 44ml/min at 273K, so we have

$$F = 44 - E$$

$$G = F * (523 / 273)$$

$$H = (G \times 10^{-6}) / (60 \times (0.2550 \times 10^{-6})), \text{ where } 0.2550 \times 10^{-6} \text{ is the area of the capillary cross section.}$$

The values in Column I are obtained through modeling with the values in Column H set as outlet boundary condition.

The values in Column J indicate how big the difference is between the required flow rate and the resulted flow rate through the annular space.

$$J = 100\% \times (I - C) / C$$

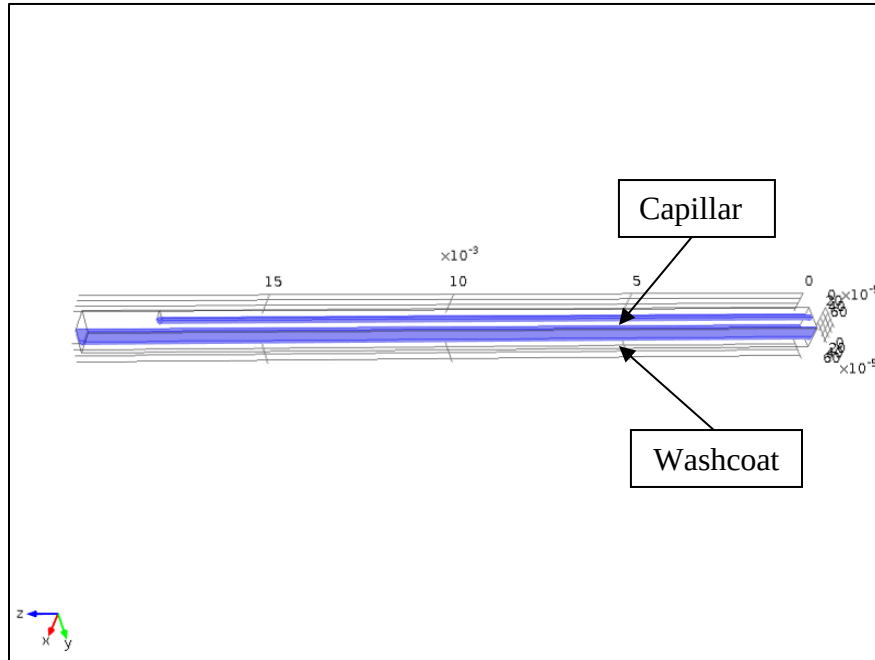


Figure AII-3(a) Capillary position at 0.2 cm

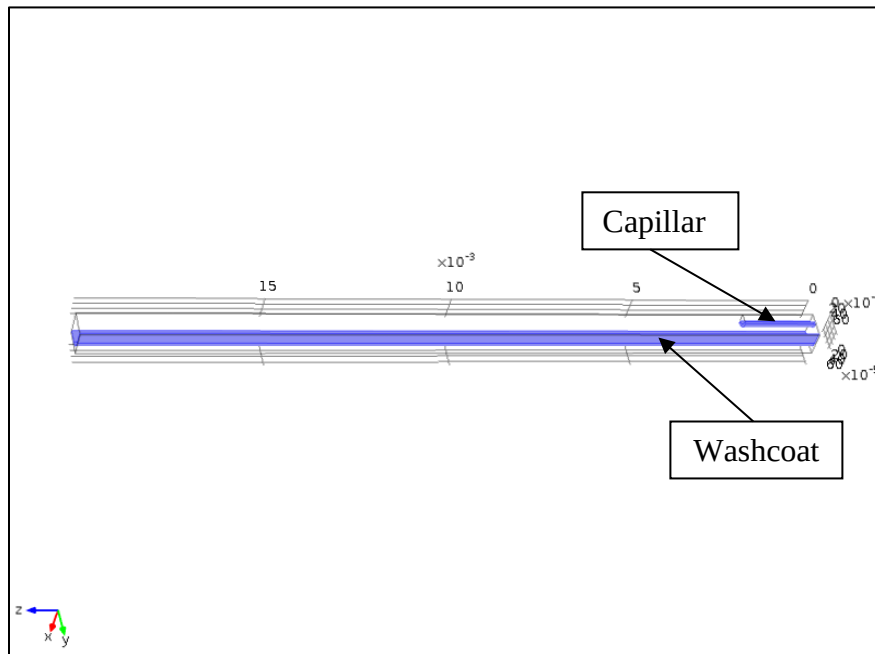


Figure AII-3(b) Capillary position at 0.18 cm

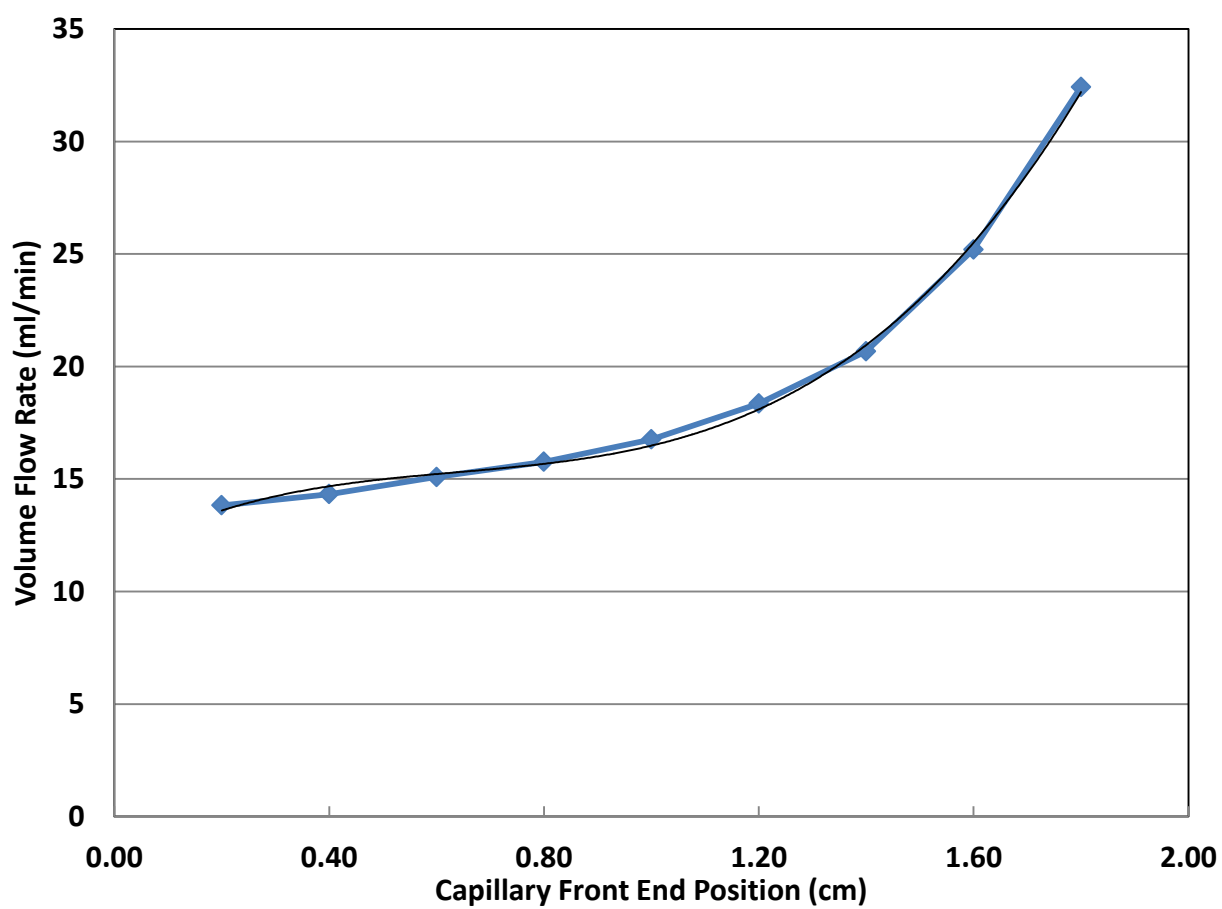


Figure AII-4 Volume flow rate through the annular space vs. capillary position at 523K

Table AII-1 Determination of sampling amount

A	B	C	D	E	F	G	H	I	J
Length of capillary in the channel (cm)	Capillary front end position (cm)	Volume flow rate through a quarter of the annular space (ml/s)	Volume flow rate through the annular space at 523K (ml/min)	Volume flow rate through the annular space at 273K (ml/min)	Volume flow rate through the capillary at 273K (ml/min)	Volume flow rate through the capillary at 523K (ml/min)	Velocity through the capillary at 523K (m/s)	Revised velocity through the annular space (m/s)	Increase in the flow rates through annular space (%)
1.800	0.200	0.05762	13.8288	7.2185	36.7815	70.4642	4.6047	0.05765	0.0520
1.600	0.400	0.05969	14.3257	7.4778	36.5222	69.9674	4.5722	0.05983	0.2339
1.400	0.600	0.06287	15.0888	7.8762	36.1238	69.2042	4.5223	0.06262	-0.3976
1.200	0.800	0.06568	15.7621	8.2276	35.7724	68.5309	4.4783	0.06584	0.2507
1.000	1.000	0.06984	16.7613	8.7492	35.2508	67.5317	4.4130	0.07043	0.8466
0.800	1.200	0.07646	18.3504	9.5787	34.4213	65.9426	4.3092	0.07665	0.2485
0.600	1.400	0.08617	20.6808	10.7951	33.2049	63.6122	4.1569	0.08680	0.7311
0.400	1.600	0.10500	25.2000	13.1541	30.8459	59.0930	3.8616	0.10440	-0.5714
0.200	1.800	0.13510	32.4240	16.9250	27.0750	51.8690	3.3895	0.13410	-0.7402

Appendix III Simulation of NH₃ Pulsing Adsorption

Simulating the process of NH₃ pulsing adsorption can help better characterize the combined effects of the processes in the system, such as flow, adsorption and desorption. The adsorption and desorption of NH₃ during pulsed adsorption was modeled, both to learn more about the process but also as an educational tool to help develop my modeling skills.

The process of NH₃ pulsing adsorption was simulated with COMSOL. Three cases for NH₃ pulsing adsorption were studied. The pulsing times examined were 30, 60 and 90 seconds. Considering the fact that gravity plays a very minor effect on the gas flow, system symmetry was again used and only a quarter of the system was modeled to reduce the calculation time.

Two subprograms, called “physics: in COMSOL, were included in the modeling, Laminar Flow and Species Transport in Porous Media. The Reynolds number for the flow through the channel was less than 2000; therefore it is appropriate to consider the flow through the channel as laminar. In the physics of Species Transport in Porous Media, the wash coat was considered as porous media. This physics can be applied to one or more species that move primarily within a fluid filling or partially filling the voids in a solid porous medium. The main feature nodes are the free flow, mobile fluid and immobile solid. The velocity field, gained from the physics of Laminar Flow, can be used as a model input. In the meantime, the equations for the species concentrations, properties of the porous media, as well as the parameters for adsorption, dispersion, and diffusion processes can be incorporated into the system.

For the physics of Laminar Flow, the governing equations and boundary conditions are shown below.

For the conservation of momentum,

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}] + \mathbf{F} \quad (\text{AIII.1})$$

Where $\mathbf{F} = 0$, ignoring the effect of gravity. As the main contents of the gas media are N₂, O₂ and CO₂, the gas properties, such as density and viscosity, can be represented by those of air.

For the conservation of mass,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (\text{AIII.2})$$

where ρ is the density of air at 523K,

μ is the viscosity of air at 523K

p is pressure

$\mathbf{I}$ is unit vector

T means vector transpose operation.

The boundary conditions are as follows.

The inlet velocity is $u = 0.4911$ m/s at 523K, and the pressure at the outlet is 1.2532×10^5 Pa.

For the physics of Species Transport in Porous Media, the system is considered to be comprised of a mobile fluid and an immobile solid. The free flow feature adds species concentrations variables and the governing equation for species transport in a free flow fluid is,

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{u}) = \nabla \cdot (D_{F,i} \nabla c_i) + R_i + S_i \quad (\text{AIII.3})$$

Here c_i is the concentration of species i , mol/m³;

$D_{F,i}$ is the fluid phase diffusion coefficient, m²/s;

R_i denotes a reaction rate expression, mol/m³·s; and

S_i is an arbitrary source term for species i , mol/(m³·s).

In the free flow feature, the solid phase was not taken into consideration. The mobile fluid, immobile solid feature adds species concentrations variables and the following equations governing species transport in a mobile fluid flowing through an immobile solid phase:

$$(\varepsilon + \rho_b k_{p,i}) \frac{\partial c_i}{\partial t} + (c_i - \rho_p c_{p,i}) \frac{\partial \varepsilon}{\partial t} + \nabla \cdot (c_i \mathbf{u}) = \nabla \cdot [(D_{D,i} + D_{e,i}) \nabla c_i] + R_i + S_i \quad (\text{AIII.4})$$

Where ε is the porosity;

ρ_b is the bulk density, $\rho_b = (1 - \varepsilon) \rho_p$;

ρ_p is the solid phase density, kg/m³;

$c_{p,i}$ is the species mass absorbed to solids, mol/kg(solid);

$D_{D,i}$ is the coefficient for dispersion, m²/s;

$D_{e,i}$ is the effective diffusion coefficient considering the effect of tortuosity and porosity, m²/s.

The governing equations for the diffusion in the thin film are:

$$-\mathbf{n} \cdot D_{s,j} \nabla c_{i,u} = \frac{D_{s,j}}{d_s} (c_{i,u} - c_{i,d}) \quad (\text{AIII.5})$$

$$-\mathbf{n} \cdot D_{s,j} \nabla c_{i,d} = \frac{D_{s,j}}{d_s} (c_{i,d} - c_{i,u}) \quad (\text{AIII.6})$$

Where d_s is the layer thickness;

$D_{s,i}$ is the diffusion coefficient in the film;

$c_{i,d}$ is the concentration of species on the surface; and

$c_{i,u}$ is the concentration of the species in the bulk phase.

As NH₃ travels through the washcoat, it can adsorb and desorb from the solid phase, which slows chemical transport through the porous medium. Adsorption and desorption reduce or increase species concentrations in the fluid. In the NH₃ pulsing adsorption only experiments, the net result

of the adsorption and desorption processes is the reduction of NH_3 concentration in the gas phase. Assuming the adsorption on the surface follows Langmuir adsorption, the physics interface predefines the following relationship to predict the solute mass absorbed to solids, c_{pi} , from the concentration in the fluid phase, c_i .

$$c_{P,i} = \frac{k_{L,i} c_{P,\max,i} c_i}{1 + k_{L,i} c_i}, \quad (\text{AIII.7})$$

$$\frac{\partial c_{P,i}}{\partial c_i} = \frac{k_{L,i} c_{P,\max,i}}{(1 + k_{L,i} c_i)^2} \quad (\text{AIII.8})$$

Where $C_{p\max}$ is the adsorption maximum, mol species per mass solid, and K_L is the Langmuir constant, m^3/mol . Dispersion is one of the factors that contribute to the mass transport as species travel through a porous medium. Local variations in pore fluid velocity lead to mechanical mixing. The dispersion occurs because fluids in pore spaces flow around solid particles, so velocities vary within pore channels. The spreading in the direction parallel or perpendicular to the flow is called longitudinal or transverse dispersion, respectively. The dispersion is assumed to be isotropic in this model.

The contribution of dispersion to the mixing of species typically dominates relative to the contribution from molecular diffusion, except when the fluid velocity is very small. The effective diffusion in porous media, D_e , depends on the structure of the porous material and the phase. For the mobile fluid, the effective diffusivity is defined as,

$$D_{e,i} = \epsilon \tau_{F,i} D_{F,i} \quad (\text{AIII.9})$$

Where $D_{F,i}$ is the single phase diffusion coefficient for the species in the fluid phase, m^2/s ;

$\tau_{F,i}$ is the tortuosity factor, unitless;

ϵ is the porosity.

An initial condition is the NH_3 initial concentration is $0 \text{ mol}/\text{m}^3$.

Boundary conditions for the Species Transport in Porous Media are,

Inlet concentration $0.009763 \text{ mol}/\text{m}^3$; and there is no flux across the walls.

The velocity distribution is shown in Figure AIII-1. The calculation result indicated that there is a velocity distribution across the radial direction. The velocity along the longitudinal central line is the largest and the along the wall is close to zero, indicating the effect of viscosity on velocity distribution.

The distribution of NH_3 concentration along the length of monolith channel is shown in Figure AIII-2, where NH_3 concentration distribution snapshots at the pulsing time of 30s, 60s, and 90s

are shown. The picture indicates the progress of NH_3 concentration in the gas phase as pulsing time increased. At the beginning of NH_3 pulsing adsorption, there was no NH_3 on the catalyst surface. The driving force for NH_3 adsorption was high and thus more NH_3 was adsorbed. As the pulse time increased, NH_3 accumulated on the catalyst surface at the front end and the driving force for NH_3 adsorption in the front decreased and more NH_3 moved to the downstream of the flow.

The quantity of adsorbed NH_3 on the catalyst surface was calculated based on the change of NH_3 concentration in the gas phase. The comparison between the experimental data and modeling NH_3 storage on the catalyst is shown in Figure AIII-3. The trends in both sets of data are pretty similar. For the storage of NH_3 at the end of the catalyst, modeling values are higher than experimental ones. This could be due to a limitation in the sampling method used in the experiment. As the NH_3 concentration became smaller at the end of the channel, and only a small portion of the flow was sampled, the detected NH_3 concentration in the gas phase for the latter part of the channel was probably approximately zero earlier than what actually was. Therefore, no NH_3 storage was calculated for the latter part of the catalyst channel in the experimental case. But it could also be due to modeling error – as there is a distribution of NH_3 adsorption strengths not accounted for. At this time, which is more accurate is not known.

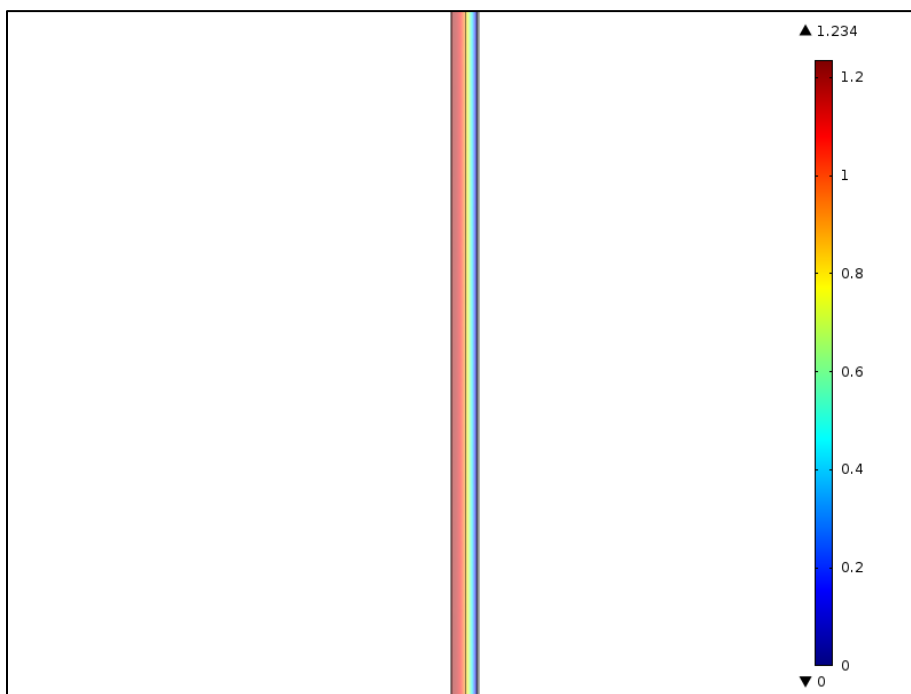


Figure AIII.1 Velocity distribution in the channel of the monolith

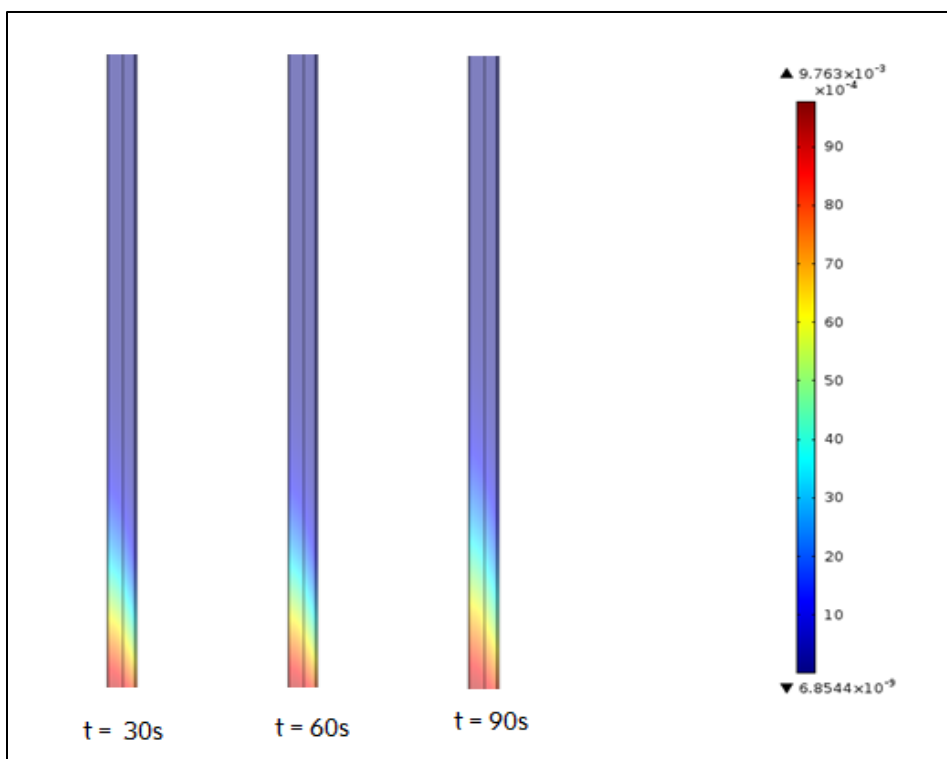


Figure AIII.2 NH_3 concentration distribution along the channel length

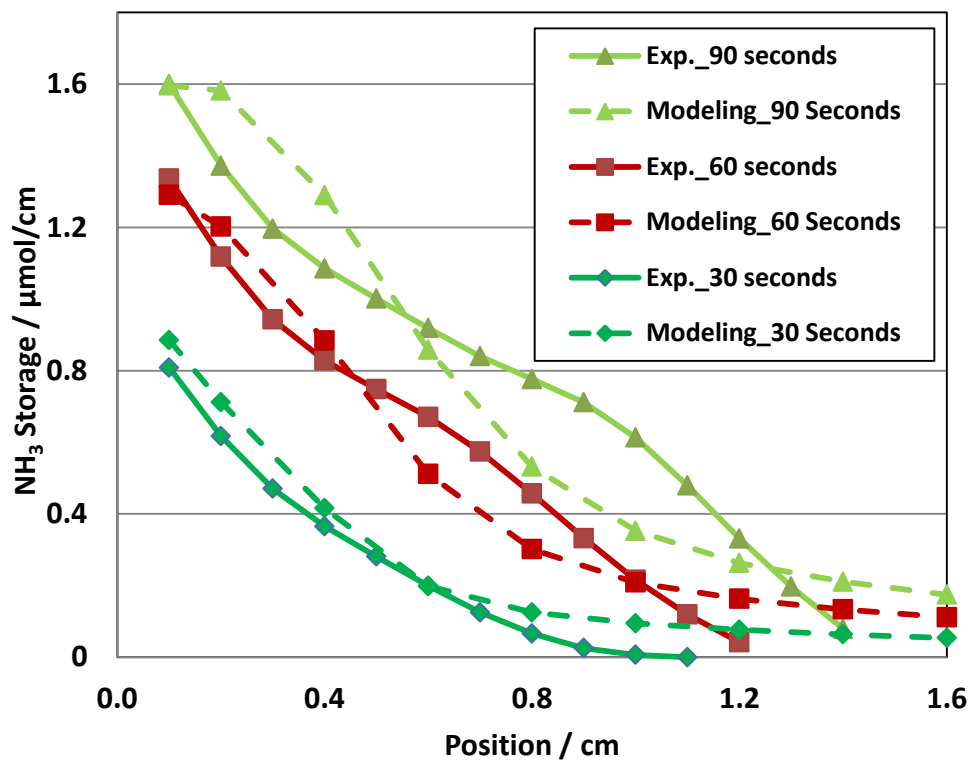


Figure AIII.3 Comparison between experimental and modeling NH_3 storage on the catalyst

Appendix IV Error Estimation

AIV.1 NH₃ TPD test

To check the repeatability of the test results for the adsorption and desorption of NH₃ on the zeolite based catalyst, repeat tests were done. The data are shown in Table AIV-1(a) and (b).

Table AIV-1(a) NH₃ adsorption and desorption on Fe-zeolite, sample 1

	NH ₃ Stored (10 ⁻³ mol)	NH ₃ Desorbed (10 ⁻³ mol)
Test 1	2.127	2.071
Test 2	2.142	2.208
Average	2.135	2.139
σ	0.011	0.097

Table AIV-1(b) NH₃ adsorption and desorption on Fe-zeolite, sample 2

	NH ₃ Stored (10 ⁻³ mol)	NH ₃ Desorbed (10 ⁻³ mol)
Test 1	2.888	2.469
Test 2	2.782	2.318
Average	2.835	2.394
σ	0.075	0.107

Both cases indicate that the test error for NH₃ adsorption is smaller than that for desorption. This is due to the fact that adsorption time is short and the detected concentration of NH₃ is relative high. For the process of desorption, the time is long and the detected concentration of NH₃ is low for the later part of the test.

AIV.2 Spatial resolution

For spatial resolution, the initial concentration of NO, NO₂, and NH₃ were taken for each level of thermal aging and temperature to make sure that the measurements of the instrument were consistent before the data were taken. As an example, the data obtained during fast SCR reaction experiments were recorded and analyzed, with data shown in Table A3-2, which indicate that the standard deviation for the NO, NO₂ and NH₃ concentration was 2.21, 4.20, and 2.23 ppm respectively.

Table AIV-2 Error estimate for NO, NO₂ and NH₃ concentration in spatial resolution tests

Temperature (°C)	NO (ppm)	NO ₂ (ppm)	NH ₃ (ppm)
179	201.5459	199.0101	392.4108
182	201.139	207.0291	397.0883
182	198.2711	199.0419	395.9665
192	198.9434	203.3502	393.3978
193	199.7898	197.224	392.3151
242	202.6119	204.4666	392.1116
245	201.3934	204.875	391.4678
246	195.3953	191.3985	388.7484
297	203.1552	203.4023	390.7637
298	200.606	201.39	390.1049
298	204.0135	206.7603	394.4622
407	203.4188	201.0086	392.9679
435	200.4255	205.4761	389.7126
435	202.1842	206.4228	393.8871
516	201.9521	201.0502	390.8603
516	202.9418	205.6196	392.2859
Average	201.1117	202.3453	392.4094
σ	2.214601	4.195845	2.225991

AIV.3 NH₃ pulsing adsorption and SCR reactions

Table AIV-3 shows an example of the error estimate in the data obtained during the NH₃ pulsing adsorption and SCR reaction tests, where NH₃ was introduced into the system in a pulse mode for 60 seconds and NO_x was introduced into the system for 30 seconds. The consumption of NO_x was detected.

Table AIV-3 Example of the error estimate for NH₃ pulsing adsorption and SCR reactions

Position (cm)	Test 1	Test 2	Test 3	Average	σ
0.1	0.36	0.42	0.38	0.38	0.030
0.2	0.34	0.37	0.31	0.34	0.030
0.3	0.32	0.28	0.35	0.32	0.035
0.4	0.30	0.26	0.37	0.31	0.055
0.5	0.30	0.29	0.37	0.32	0.044
0.6	0.30	0.30	0.33	0.31	0.018
0.7	0.28	0.28	0.28	0.28	0.004
0.8	0.23	0.21	0.24	0.23	0.016
0.9	0.17	0.14	0.21	0.17	0.030
1.0	0.14	0.11	0.17	0.14	0.026
1.1	0.12	0.11	0.13	0.12	0.009
1.2	0.10	0.11	0.10	0.11	0.007
1.3	0.07	0.11		0.09	0.030

The data show that the test errors for NH₃ pulsing adsorption and SCR reactions were fairly large. In order to reduce the impact of error, dense points were inspected and tests were repeated and average values were taken to describe the profiles of NH₃ storage or NO_x conversion.

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REFERENCES

1. <http://www.epa.gov/apti/course422/apc1.html>
2. A.C. Stern, H.C. Wohlers, R.W. Boubel, W.P. Lowry, *Fundamental of Air Pollution*, Academic Press, New York, 1973.
3. V. I. PaÅrvulescua, P. Grangeb, B. Delmon, *Catalysis Today*, 46(1998)233.
4. M. Z. Jacobson, *Atmospheric Pollution, History, Science, and Regulation*, Cambridge University Press, 2002.
5. T. Miyadera, *Applied Catalysis B: Environmental*, 2(1993)199.
6. A. Grossale, I. Nova, E. Tronconi, D. Chatterjee, M. Weibel, *Journal of Catalysis*, 256(2008)312.
7. H. Sjøvall, L. Olsson, E. Fridell, R.J. Blint, *Applied Catalysis B: Environmental*, 64(2006)180.
8. I. E. Wachs, G. Deo, B. M. Weckhuysen, A. Andreini, M. A. Vuurman, M. de Boer, M. D. Amiridis, *Journal of Catalysis*, 161(1996)211.
9. W. Addy Majewski, http://www.dieselnets.com/tech/cat_scr_mobile.html
10. J. Gibson, O. Groene, *Automotive Engineering*, October(1991)18.
11. H. T. Hug, A. Mayer, A. Hartenstein, *SAE Technical Paper*, 930363.
12. C. B. Weaver, C. S. McGreger, *SAE Technical Paper* 940453, 1994.
13. C. Havenith, R. P. Verbeek, D. M. Heaton, P. van Sloten, *SAE Technical Paper*, 952652.
14. C. Havenith, R. P. Verbeek, *SAE Technical Paper*, 970185.
15. H. Laxders, R. Backes, G. Haxthwohl, D. A. Ketcher, R. W. Horrocks, R. G. Hurley, R. H. Hammerle, *SAE Technical Paper*, 952493.
16. R. Hammerle, US DOE, 9th Diesel Engine Emission Reduction Conference (DEER), Newport, RI, August 2003.
17. A. P. Walker, D. Manning, L. Bernegger, R. Allansson, P. G. Blakeman, M. Lavenius, A. J. Uusimäki, S. Erkkfeldt, H. Landa, B. Ball, P. Harrod, *SAE Technical Paper*, 2003-01-0778.
18. P. Gabrielsson, I. Gekas, L. Nyengaard, T. Lund, *SAE Technical Paper* 2002-01-0289.
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20. S. Hackenberg, M. Ranalli, *SAE Technical Paper*, 2007-01-1239.
21. E.C. Corbos; M. Haneda; X. Courtois; P. Marecot; D. Duprez; H. Hamada, *Applied Catalysis A: General*, 365(2009)187.
22. N. V. Heeb, A-M. Forss, S. Bruhlmann, R. Luscher, C. J. Saxer, P. Hug, *Atmospheric Environment*, 40(2006)5986.

23. N. V. Heeb, C. J. Saxer, A-M. Forss, S. Bruhlmann, *Atmospheric Environment*, 42(2008)2543.
24. T. Huai, T. H. Durbin, J. Waynemiller, J. Pisano, C. G. Sauer, S. H. Rhee, J. M. Norbeck, *Environmental Science and Technology*, 37(2003)4841.
25. T. Huai, T. D. Durbin, T. Younglove, G. Scora, M. Barth, J. M. Norbeck, *Environmental Science and Technology*, 39(2005)9595.
26. P. Forzatti, L. Lietti, N. Gabrielli, *Applied Catalysis B: Environmental*, 99 (2010) 145.
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28. L. Lietti, I. Nova, P. Forzatti, *Journal of Catalysis*, 257(2008)270.
29. W. Li, K. L. Perry, K. Narayanaswamy, C. H. Kim and P. Najt, *SAE Technical Paper*, 2010-01-0366.
30. P. Forzatti, *Applied Catalysis A: General*, 222(2001)221.
31. M.D. Amiridis, T. Zhang, R.J. Farrauto, *Applied Catalysis B: Environmental*, 10(1996)203.
32. M. Kang, D.J. Kim, E.D. Park, J.M. Kim, J.E. Yie, S.H. Kim, L. Hope-Weeks, E.M. Eyring, *Applied Catalysis B: Environmental*, 68(2006)21.
33. F. Acke, M. Skoglundh, *Applied Catalysis B: Environmental* 20(1999)133.
34. R. M. Heck, *Catalysis Today*, 53(1999)519.
35. I. Nova, L. Lietti, E. Tronconi, P. Forzatti, *Catalysis Today*, 60(2000)73.
36. G. Busca, L. Lietti, G. Ramis, F. Berti, *Applied Catalysis B: Environmental* 18(1998)1.
37. N. Apostolescu, B. Geiger, K. Hizbullah, M.T. Jan, S. Kureti, D. Reichert, F. Schott, W. Weisweiler, *Applied Catalysis B: Environmental*, 62(2006)104.
38. R. Q. Long, R. T. Yang, *Journal of Catalysis*, 188(1999)332.
39. G. Xie, Z. Liu, Z. Zhu, Q. Liu, J. Ge, Z. Huang, *Journal of Catalysis*, 224(2004)42.
40. C. Cristiani, P. Forzatti, G. Busca, *Journal of Catalysis*, 116(1989)586.
41. G. Busca, *Materials Chemistry & Physics* 19(1988)157.
42. M. Iwamoto; H. Hamada, *Catalysis Today*, 10(1991)57.
43. <http://www.3dchem.com/molecules.asp?ID=86#>
44. WO2008/132452 A2.
45. US 7,601,662 B2, Oct. 13, 2009.
46. T. Ishihara, M. Kagawa, F. Hadama, Y. Takita, *Journal of Catalysis*, 169(1997)93.
47. D. W. Fickel, E. D'Addio, J. A. Lauterbach, R. F. Lobo, *Applied Catalysis B: Environmental*, 102(2011)441.
48. X. Feng, W. K. Hall, *Journal of Catalysis*, 166(1997)368.

49. S. Ashtekar, S. V. V. Chilukuri, D. K. Chakrabarty, *Journal of physical Chemistry*, 98(1994)4878.
50. S. I. Zones, L. T. Yuen, S. J. Miller, U. S. Patent 6709644(2004).
51. J.H. Kwak, R.G. Tonkyn, D.H. Kim, J. Szanyi, C.H.F. Peden, *Journal of Catalysis*, 275 (2010)187.
52. M. Koebel, G. Madia, M. Elsener, *Catalysis Today*, 73(2002)239.
53. Y. S. Mok, Y. J. Huh, *Plasma Chemistry and Plasma Processing*, Vol. 25, No. 6, December 2005.
54. K. Kamasamudram, N. W. Currier, X. Chen, A. Yezerets, *Catalysis Today*, 151(2010)212.
55. S. J. Schmieg, S. H. Oh, C. H. Kim, D. B. Brown, J. H. Lee, C. H.F. Peden, D. H. Kim, *Catalysis Today*, 184(2012)252.
56. G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur, R.J. Willey, *Journal of Catalysis*, 157(1995)523.
57. L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, P. Forzatti, F. Bregani, *Journal of Catalysis*, 187(1999)419.
58. M. Takagi, T. Kowai, M. Soma, T. Onishi, K. Tamaru, *Journal of Catalysis*, 50(1977)441.
59. A. Miyamoto, K. Kobayashi, M. Inomata and Y. Murakami, *Journal of Physical Chemistry*, 86(1982)2945.
60. J.P. Chen, R.T. Yang, *Applied Catalysis A: General*, 80 (1992) 135.
61. N.Y. Topsoe, *Journal of Catalysis*, 128(1991)499.
62. N.Y. Topsoe, J.A. Dumesic; H. Topsoe, *Journal of Catalysis*, 151(1995)241.
63. H. Schneider, S. Tschudin, M. Schneider, A. Wokaun and A. Baiker, *Journal of Catalysis*, 147(1994)5.
64. N.Y. Topsoe, *Science*, 265 (1994) 1217.
65. J. Eng; C. H. Bartholomew, *Journal of Catalysis*, 171(1997)14.
66. J.G. Amores, V.S. Escibano, G. Ramis, G. Busca, *Applied Catalysis B: Environmental*, 13(1997)45.
67. L. Lietti, J. Svachula, P. Forzatti, G. Busca, G. Ramis and F. Bregani, *Catalysis Today*, 17(1993)131.
68. E. Tronconi, L. Lietti, P. Forzatti, S. Malloggi, *Chemical Engineering Science*, 51(1996)2965.
69. E.-Y. Choi; I.-S. Nam ; Y. G. Kim, *Journal of Catalysis*, 161(1996)597.

70. H.Y. Huang, R.Q. Long, R.T. Yang, *Applied Catalysis A: General* 235(2002)241.
71. Z. Li, L. Shen, W. Huang, Ke-chang Xie, *Journal of Environmental Sciences*, 19(2007)1516.
72. E. Tronconi, I. Nova, C. Ciardelli, D. Chatterjee, M. Weibel, *Journal of Catalysis*, 245 (2007) 1.
73. S. Kieger; G. Delahay; B. Coq; B. Neveu, *Journal of Catalysis*, 183(1999)267.
74. G. Delahay, B. Coq, S. Kieger, B. Neveu, *Catalysis Today* 54(1999)431.
75. T. Komatsu, M. Nunokawa, I.S. Moon, T. Takahara, S. Namba, T. Yashima, *Journal of Catalysis*, 148(1994)427.
76. A.-Z. Ma, W. Grunert, *Chemical Communications*, (1999)71.
77. G. Centi, S. Perathoner, D. Biglino, E. Giamello, *Journal of Catalysis* 152(1995)75.
78. J. Y. Kim, G. Cavataio, J. E. Patterson, P. M. Laing, C. K. Lambert; SAE Technical Paper, 2007-01-1573.
79. A. Grossale, I. Nova, E. Tronconi, *Journal of Catalysis*, 265(2009)141.
80. W.C. Wong, K. Nobe, *Industrial & Engineering Chemistry Product Research and Development*, 23(1984)564.
81. V. I. Marshneva, E.M. Slavinskaya, O.V. Kalinkina, G.V. Odegova, E.M. Moroz, G.V. Lavrova, A.N. Salanov, *Journal of Catalysis*, 155(1995)171.
82. M. Kang, E.D. Park, J.M. Kim, J.E. Yie, *Catalysis Today*, 111(2006)236.
83. R. Matarrese, H. H. Ingelsten, M. Skoglundh, *Journal of Catalysis*, 258(2008)386.
84. I. Nova, L. Castoldi, L. Lietti, E. Tronconi, P. Forzatti, *Topics in Catalysis*, 42–43(2007)21.
85. M. Colombo, I. Nova, E. Tronconi, *Catalysis Today*, 197(2012)243.
86. M. Koebel, M. Elsener, G. Madia, *Industrial & Engineering Chemistry Research*, 40(2001)52.
87. M. Koebel, G. Madia, F. Raimondi, A. Wokaun, *Journal of Catalysis*, 209(2002)159.
88. C. Ciardelli; I. Nova; E. Tronconi; D. Chatterjee; B. Bandl-Konrad; M. Weibel; B. Krutzsch, *Applied Catalysis B: Environmental*, 70(2007)80.
89. http://www.dieselnet.com/tech/cat_scr_mobile.html
90. M. Schwidder, S. Heikens, A.D. Toni, S. Geisler, M. Berndt, A. Brückner, W. Grünert, *Journal of Catalysis*, 259(2008)96.
91. J. Girard, R. Snow, G. Cavataio, C. Lambert, SAE Technical Paper, 2007-01-1581.
92. L. Olsson, H. Sjövall, R. J. Blint, *Applied Catalysis B: Environmental*, 87(2009)200.

93. P.S. Metkar, N. Salazar, R. Muncrief, V. Balakotaiah, M. P. Harlod, *Applied Catalysis B: Environmental*, 104(2011)110.
94. M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, N. Söger, M. Pfeifer, Y. Demel, L. Mussmann, *Applied Catalysis B: Environmental*, 67(2006)187.
95. A. Grossale, I. Nova, E. Tronconi, *Catalysis Today*, 136(2008)18.
96. S.S. Mulla, N. Chen, L. Cumananunge, W.N. Delgass, W.S. Epling, F.H. Ribeiro, *Catalysis Today*, 114(2006)57.
97. J. Despres, M. Koebel, O. Krocher, M. Elsener, A. Wokaun, *Microporous and Mesoporous Materials*, 58(2003)175.
98. N. Wilken, K. Wijayanti, K. Kamasamudram, N. W. Currier, R. Vedaiyan, A. Yezerets, L. Olsson, *Applied Catalysis B: Environmental*, 111– 112(2012)58.
99. M. H. Kim, I.-S. Nam, Y. G. Kim, *Journal of Catalysis*, 179(1998)350.
100. R.G. Silver, M.O. Stefanick, B.I. Todd, *Catalysis Today*, 136(2008)28.
101. Z. Huang, Z. Zhu, Z. Liu, *Applied Catalysis B: Environmental*, 39(2002)361.
102. Z.P. Zhu, H.X. Niu, Z.Y. Liu, S.J. Liu, *Journal of Catalysis*, 195(2000)268.
103. Y. Cheng, C. Lambert, D. H. Kim, J. H. Kwak, S. J. Cho, C. H.F. Peden, *Catalyst Today*, 151(2010)266.
104. J.A. Sullivan, J. Cunningham, M.A. Morris, K. Keneavey, *Applied Catalysis B: Environmental* 7(1995)137.
105. M. Shelef, C.N. Montreuil, H.W. Jen, *Catalysis Letters*, 26(1994)277.
106. H. Sjoval, R. J. Blint, L. Olsson, *The Journal of Physical Chemistry C*, 113(2009)1393.
107. P. Balle; B. Geiger; S. Kureti, *Applied Catalysis B: Environmental*, 85(2009)109.
108. J.A.Z. Pieterse, R.W. van den Brink, S. Booneveld, F.A. de Bruijn, *Applied Catalysis B: Environmental* 39(2002)167.
109. R.A. Grinsted, H.-W. Jen, C.N. Montreuil, M.J. Rokosz, M. Shelef, *Zeolites*, 13(1993)602.
110. J. O. Petunchi, W. K. Hall, *Journal of Catalysis*, 80(1983)403.
111. J. H. Park, H. J. Park, J. H. Baik, I. S. Nam, C. H. Shin, J. H. Lee, B. K. Cho, S. H. Oh, *Journal of Catalysis*, 240(2006)47.
112. A. V. Kucherov, C. P. Hubbard, M. Shelef, *Journal of Catalysis*, 157(1995)603.
113. K.C.C. Kharas, H.J. Robota, D.J. Liu, *Applied Catalysis B: Environmental*, 2(1993)225.
114. K. Krishna, M. Makkee, *Catalysis Today*, 114(2006)23.
115. J. H. Kwak, D. Tran, S. D. Burton, J. Szanyi, J. H. Lee, C. H.F. Peden, *Journal of Catalysis*, 287(2012)203.

116. G. Cavataio, J. R. Warner, J. W. Girard, J. Ura, D. Dobsonand, C. K. Lambert, SAE Technical Paper, 2009-01-0903.
117. J-Y. Luo, H. Oh, C. Henry, W. Epling, Applied Catalysis B: Environmental, 123–124(2012)296.
118. I. Heo, Y. Lee, I.S. Nam, J.W. Choung, J.H. Lee, H.J. Kim, Microporous and Mesoporous Materials, 14(2011)8.
119. J.H. Li, R.H. Zhu, Y.S. Cheng, C.K. Lambert, R.T. Yang, Environmental Science and Technology, 44 (2010)1799.
120. C. He, Y. Wang, Y. Cheng, C.K. Lambert, R.T. Yang, Applied Catalysis A: General, 368 (2009)121.
121. I. Malpartida, O. Marie, P. Bazin, M. Daturi, X. Jeandel, Applied Catalysis B: Environmental, 102(2011)190.
122. M. Devarakonda, R. Tonkyn, D. Herling, SAE Technical Paper, 2010-01-1171.
123. C. Montreuil, C. Lambert, SAE Technical Paper, 2008-01-1030.
124. A. Sultana, T. Nanba, M. Sasaki, M. Haneda, K. Suzuki, H. Hamada, Catalysis Today, 164(2011)495.
125. T. Nanba, A. Sultana, S. Masukawa, M. Haneda, J. Uchisawa, A. Obuchi, H. Hamada, Topics in Catalysis, 52(2009)1766.
126. J. Girard, R. Snow, G. Cavataio, C. Lambert, SAE Technical Paper, 2008-01-0767.
127. A. Sultana, T. Nanba, M. Haneda; H. Hamada, Catalysis Communications, 10(2009)1859.
128. S. D. Yim, S. J. Kim, J. H. Baik, I.–S. Nam, Y. S. Mok, J.-H. Lee; B. K. Cho, S. H. Oh, Industrial& Engineering Chemistry Research, 2004(43)4856.
129. J. H. Baik, S. D. Yim, I.-S. Nam, Y. S. Mok, J-H. Lee, B. K. Cho, S. H. Oh, Industrial & Engineering Chemistry Research, 45(2006)5258.
130. L. Olsson, H. Sjövall, R.J. Blint, Applied Catalysis B: Environmental, 81(2008)203.
131. H. Sjövall, R. J. Blint, L. Olsson, Applied Catalysis B: Environmental, 92(2009)138.
132. W.B. Williamson, D.R. Flentge, J.H. Lunsford, Journal of Catalysis, 37(1975)258.
133. W.B. Williamson, J.H. Lunsford, Journal of Physical Chemistry, 80(1976)2664.
134. A. Cybulski, J. A. Moulijn, Catalysis Reviews: Science and Engineering, 36 (1994) 179.
135. M. Shelef, R. W. McCabe, Catalysis Today, 62(2000)35.
136. M. Colombo, I. Nova, E. Tronconi, Chemical Engineering Science, 75(2012)75.
137. A. Scheuer, M. Votsmeier, A. Schuler, J. Gieshoff, A. Drochner and H. Vogel, Topics in Catalysis, 52(2009)1847.

138. N.V. Heeb, A-M Forss, S. Bruhlmann, R. Luscher, C.J. Saxer, P. Hug, *Atmospheric Environment*, 40(2006)5986.
139. C. H. Kim, K. Perry, M. Viola, W. Li, K. Narayanaswamy, SAE Technical Paper, 2011-01-0306.
140. D. Chatterjee, P. Koci, V. Schmeisser, M. Marek, M. Weibel, SAE Technical Paper, 2010-01-0887.
141. O. Guralp, G. Qi, W. Li, P. Najt, SAE Technical Paper, 2011-01-0307.
142. O. Shakir, A. Yezerets, N.W. Currier, W.S. Epling, *Applied Catalysis A: General*, 365(2009)301.
143. J. Choi, W.P. Partridge, J.A. Pihl, C.S. Daw, *Applied Catalysis A: General*, 293(2005)24.
144. R. Horn, N. J. Degenstein, K. A. Williams, L. D. Schmidt, *Catalysis Letters*, 110(2006)169.
145. J. Choi, W.P. Partridge, J.A. Pihl, C.S. Daw, *Catalysis Today*, 136(2008)173.
146. J. Choi, W. P. Partridge, C. S. Daw, *Applied Catalysis B: Environmental* 77(2007)145.
147. V.Y. Prikhodko, K. Nguyen, J.S. Choi, C.S. Daw, *Applied Catalysis B: Environmental*, 92 (2009) 9.
148. A. Bitsch-Larsen, N.J. Degenstein, L.D. Schmidt, *Applied Catalysis B: Environmental*, 78(2008)364.
149. A. Russel, W.S. Epling, H. Hess, H.Y.Chen, C. Henry, N.W. Currier, A. Yezerets, *Industrial& Engineering Chemistry Research*, 49(2010)10311.
150. J-S. Choi, W. P. Partridge, J. A. Pihl, M-Y. Kim, P. Koci, C. S. Daw, *Catalysis Today*, 184(2012)20.
151. K. Irani, W.S. Epling, R. Blint, *Topics in Catalysis*, 52(2009)1856.
152. C. Henry, K. Kamasamudram, N. Currier, A. Yezerets, M. Castagnola, H-Y. Chen, SAE Technical Paper, 2012-01-1084.
153. T. V. Johnson, *Platinum Metals Review*, 52(2008)23.
154. T.V. Johnson, SAE Technical Paper, 2009-01-0121.
155. Y. Kodama, V.W. Wong, SAE Technical Paper, 2010-01-1071.
156. G. Cavataio, J. Girard, J.E. Patterson, C. Montreuil, Y. Cheng, C.K. Lambert, SAE Technical Paper, 2007-01-1575.
157. K. Kamasamudram, N.W. Currier, T. Szailer, A. Yezerets, SAE Technical Paper, 2010-01-1182.
158. A. Crossale, I. Nova, E. Tronconi, D. Chatterjee, M. Weibel, *Topics of Catalysis*, 52 (2009)1837.

159. A. Crossale, I. Nova, E. Tronconi, D. Chatterjee, M. Weibel, *Topics of Catalysis*, 52 (2009)1837.
160. M. Colombo, I. Nova, E. Tronconi, *Catalysis Today*, 151(2010)223.
161. M. Schaefer, L. Hofmann, P. Girot, R. Rohe, *SAE Technical Paper*, 2009-01-0912.
162. A. Donazzi, B.C. Michael, L.D. Schmidt, *Journal of Catalysis*, 260(2008)271.
163. J.S. Choi, W.P. Partridge, C.S. Daw, *Applied Catalysis A: General*, 293(2005)24.
164. J.S. Choi, W.P. Partridge, C.S. Daw, *Applied Catalysis B: Environmental*, 77(2007)145.
165. M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, G. Mitrikas, N. Söger, M. Pfeifer, Y. Demel, L. Mussmann, *Catalysis Today*, 119(2007)137.
166. M. Høj, M.J. Beier, J.D. Grunwaldt, S. Dahl, *Applied Catalysis B: Environmental*, 93(2009)166.
167. J.M. Fedeyko, B. Chen, H.Y. Chen, *Catalysis Today*, 151(2010)231.
168. M. Iwasaki, H. Shinjoh, *Journal of Catalysis*, 273(2010)29.
169. M. Iwasaki, K. Yamazaki, H. Shinjoh, *Applied Catalysis A: General*, 366(2009)84.
170. S. Brandenberger, O. Kröcher, A. Wokaun, A. Tissler, R. Althoff, *Journal of Catalysis*, 268(2009)297.
171. A. Savara, M. J. Li, W. M. N. Sachtler, E. Weitz, *Applied Catalysis B: Environmental*, 81(2008)251.
172. S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, *Applied Catalysis B: Environmental*, 95(2010)348.
173. M. Wallin, C.J. Karlsson, M. Skoglundh, A. Palmqvist, *Journal of Catalysis*, 218(2003)354.
174. R.Q. Long, R.T. Yang, *Journal of Catalysis*, 207(2002)224.
175. W. S. Epling, "Diesel Emissions Control Catalysis", *Catalysis Today*, 151(2010)201.
176. K. Rahkamaa-Toloen, M.L. Maunula, M. Huuhtanen, and R.L. Keiski, *Catalysis Today*, 100(2005)217.
177. T.J. Toops, K. Nguyen, A.L. Foster, B.G. Bunting, N.A. Ottinger, J.A. Pihl, E.W. Hagaman, J. Jiao, *Catalysis Today* 151(2010)257.
178. Y. He, D. B. Brown, S. Lu, S. M. J. Paratore, J. Li, *SAE Technical Paper*, 2009-01-0274.
179. S.J. Schmieg, J.-H. Lee, *SAE Technical Paper*, 2005-01-3881.
180. G. Qi, Y. Wang, R.T. Yang, *Catalysis Letters*, 111(2008)121.
181. G. Qi, R.T. Yang, R. Chang, S. Cardoso, and R.A. Smith, *Applied Catalysis A: General*, 207(2004)275.

182. J.H. Park, H.J. Park, J.H. Baik, I.S. Nam, C.H. Shin, J.H. Lee, B.K. Cho, S. H. Oh, *Journal of Catalysis*, 240(2006)47.
183. I. Bull, W. Xue, P. Burk, R. Boorse, W. Jaglowski, G. Koermer, A. Moini, J. Patchett, J. Dettling, M. Caudle, US Patent 7,601,662 Issued 13 October 2009.
184. J.C. Volta, J.L. Portefaix, *Applied Catalysis*, 18(1985)1.
185. N. Wilken, K. Kamasamudram, N.W. Currier, J. Li, A. Yezerets, and L. Olsson, *Catalysis Today*, 151(2009)237.
186. H. Sjoval, L. Olsson, E. Fridell, R.J. Blint, *Applied Catalysis B: Environmental*, 180(2006)64.
187. G. Delahay, S. Kieger, N. Tanchoux, P. Trens, and B. Coq, *Applied Catalysis B: Environmental*, 52(2004)251.
188. K.C. Taylor, "Automobile catalytic converters," in *Catalysis Science and Technology* edited by J.R. Anderson and M. Boudart, Vol. 5, (Springer-Verlag, New York, 1984).
189. J. Luo, X. Hou, P. Wijayakoon, S.J. Schmieg, W. Li, W.S. Epling, *Applied Catalysis B: Environmental*, 102(2011)110.
190. X. Hou, W. S. Epling, S. J. Schmieg, W. Li, SAE Technical Paper, 2011-01-1138.
191. J. Andersen, E. Bailie, L. Casci, H. Chen, M. Fedeyko, S. Foo and R. Rajaram, WO 2008/132452 A2. International Publication Date 6 November 2008.
192. L. Lietti; I. Nova; G. Ramis; L. Dall'Acqua; G. Busca; E. Giamello; P. Forzatti; F. Bregani, *Journal of Catalysis*, 187(1999)419.
193. Y. H. Yeom, J. Henao, M. J. Li, W. M. H. Sachtler, E. Weitz, *Journal of Catalysis*, 231(2005)181.