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 NOx, particulate matter and unburned hydrocarbons. Selective catalytic reduction (SCR) catalysis is likely the best choice for NOx control. In SCR, NH\textsubscript{3} selectively reacts with NOx to form N\textsubscript{2} – the selectivity refers to NH\textsubscript{3} reacting with NOx instead of the abundant O\textsubscript{2}. Urea is used as the NH\textsubscript{3} source, being injected into the exhaust as an aqueous solution where the urea decomposes and NH\textsubscript{3} 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 NH\textsubscript{3} 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 (2NO + 2NH\textsubscript{3} + 1/2O\textsubscript{2} = 2N\textsubscript{2} + 3H\textsubscript{2}O), the fast SCR reaction (NO + NO\textsubscript{2} + 2NH\textsubscript{3} = 2N\textsubscript{2} + 3H\textsubscript{2}O), and NO\textsubscript{2}-SCR, (6NO\textsubscript{2} + 8NH\textsubscript{3} = 7N\textsubscript{2} + 12H\textsubscript{2}O). Results show that in the presence of NO\textsubscript{2}, but at a NO\textsubscript{2}/NOx ratio < 0.5, the fast SCR reaction proceeds followed by the standard SCR reaction, i.e. in series. If the NO\textsubscript{2}/NOx ratio exceeds 0.5, the NO\textsubscript{2}-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, NH\textsubscript{3} oxidation, and the reduction reactions, were studied. Last but not least, for the purpose of passive SCR system development, transient NH\textsubscript{3} storage profiles along the monolith channel were measured with SpaciFTIR. Passive SCR is a system where the NH\textsubscript{3} is generated on an upstream catalyst, such as a three-way catalyst or lean-NOx trap, instead of via urea injection. In such a system, NH\textsubscript{3} is therefore not constantly being fed to the SCR catalyst, but “arrives” in pulses. Factors such temperature, NH\textsubscript{3} concentration, pulsing time, flow rate and thermal aging were investigated. For the first time, NH\textsubscript{3} 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, craftsmen'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 NOx pollution

NOx 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-NOx-Ox, 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 NOx from automobiles

Automobiles are a significant contributor of NOx pollutants, with the NOx originating from the reaction between N₂ and O₃ during the high temperature combustion process. NOx 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, NOx control from gasoline engine emissions has been mainly accomplished using a three-way catalyst (TWC), with which hydrocarbons, CO and NOx are oxidized and reduced. Thanks to its high energy efficiency, the diesel engine is becoming more common. In order to reduce NOx 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 NOx in an oxidizing environment. An example of NOx 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 NOx produced. NOx 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 NOx catalytically, for example via catalytic reduction. The focus of this thesis is selective catalytic reduction (SCR) of NOx in diesel engine exhaust. The reductant is NH₃, which can be added into the system or produced over an upstream TWC or Lean NOx Trap (LNT).

1.4 Selective catalytic reduction (SCR)
Diesel engines produce exhaust containing a large excess of O₂, so NOx reduction to N₂ in the O₂-rich exhaust demands a catalyst that can reduce NOx selectively. The SCR process is based on the selective reaction between NOx 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 NOx reduction in the presence of excess O₂. Ag/Al₂O₃ is effective for the SCR of NOx by hydrocarbons, in particular with C₂H₅OH [5]. NH₃ is very effective for NOx reduction over Fe- and Cu-zeolites [6-7]. SCR of NOx 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 NOx 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 NOx 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 NOx trap (LNT) [19-21], where the SCR catalyst is placed downstream to make use of the NH\textsubscript{3} 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 NOx. Most predictions indicate SCR will become typical for diesel engine exhaust gas cleanup, and may even move into the lean-burn gasoline markets in the future.

Early studies showed that when NOx is reduced over TWCs and LNT catalysts, NH\textsubscript{3} could be formed. [22-28] Based on such findings, the concept of passive NH\textsubscript{3} SCR was recently proposed [29], where NH\textsubscript{3} is produced during fuel-rich operation, via reduction of the NOx over the TWC, or LNT. The produced NH\textsubscript{3} is then stored on the downstream SCR catalyst, and can be used as the reductant to reduce NOx 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 NOx 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 NH\textsubscript{3} storage and oxidation, NO oxidation, and finally on general performance.
- Evaluating NH\textsubscript{3} adsorption in a passive NH\textsubscript{3} SCR system, including how the adsorbed distribution is affected by temperature, time and concentration, and how SCR reactions are affected by the NH\textsubscript{3} 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 NH\textsubscript{3} 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. NH\textsubscript{3} pulsing adsorption in a passive NH\textsubscript{3}
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 DeNOx 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/Al$_2$O$_3$, which have shown significant activity, with the temperature window for NOx conversion in relatively low temperature ranges [30]. They have, however, the disadvantage of producing relatively high amounts of byproduct N$_2$O [31] at low temperature and an enhanced activity toward NH$_3$ 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 NOx control from stationary sources [34-35]. A typical example formulation is V$_2$O$_5$/WO$_3$-TiO$_2$. 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 NOx reduction activity [36]. The main drawback of this catalyst is that it is easily poisoned by SO$_2$. Furthermore, at high temperatures, the catalyst is active in the oxidation of SO$_2$ to SO$_3$, which results in a rapid decrease in SCR activity and selectivity. Finally, vanadia will sublimate 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, TiO$_2$ is chosen as the vanadia support because TiO$_2$-based industrial catalysts are only partially, and reversibly, sulfated in the presence of SO$_2$, and under certain conditions the S exposure can even enhance the SCR catalytic activity [39]. Another advantage of using TiO$_2$ is that on the anatase phase of TiO$_2$, vanadium oxide can be well dispersed, giving rise to “isolated” vanadyl centers, which are more reactive [40-41]. MoO$_3$ and WO$_3$ are usually added both as stabilizers and as promoters [35] to vanadia-based SCR catalysts and possibly as SO$_2$ 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 NOx 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 NOx 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 NOx 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 NOx 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 NOx, the second reaction listed above occurs, and it is more rapid than the first. Therefore, a catalyst’s ability to modify the NO₂/NOx 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:

\[ 2NO + O_2 \rightarrow 2NO_2 \quad \Delta H^\circ = -115.44 \text{ kJ} \quad (2.4) \]

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 NOx conversion, with oxidation reactions listed as follows:

\[ 4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad \Delta H^\circ = -1267.31 \text{ kJ} \quad (2.5) \]
\[ 4NH_3 + 7O_2 \rightarrow 4NO + 6H_2O \quad (2.6) \]
\[ 4NH_3 + 5O_2 \rightarrow 4NO_2 + 6H_2O \quad (2.7) \]
\[ 2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad (2.8) \]

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]:

\[ 2NH_3 + 2NO_2 \rightarrow N_2O + N_2 + 3H_2O \quad (2.9) \]
\[ 4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \quad (2.10) \]

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 NOx conversion under different driving modes was investigated. Using coverage-dependent NOx 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 \( \text{NH}_3 \) as the reducing agent, the mechanism of \( \text{NH}_3 \) adsorption and activation, standard SCR and fast SCR reactions have been studied. Together with those topics, studies on the role of \( \text{NO}_2 \), \( \text{NH}_3 \) oxidation and NO oxidation are also reviewed below.

### 2.3.1 \( \text{NH}_3 \) adsorption and activation

Regarding \( \text{NH}_3 \) 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 \( \text{NH}_3 \) 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 \( \text{NH}_3 \) 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 \( \text{NH}_3 \) is protonated as a \( \text{NH}_4^+ \) 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 \( \text{NH}_3 \) species over vanadia-based catalysts are \( \text{NH}_4^+ \) ions, so activation of \( \text{NH}_3 \) would occur on the catalyst surface Brønsted acid sites. Several other authors supported a key role of Brønsted acid sites in producing \( \text{NH}_4^+ \) ions as active \( \text{NH}_3 \) species, although with different reaction schemes [60-64]. However, there is disagreement on the activation mode of \( \text{NH}_3 \) over the catalysts, as discussed below.

Regarding the coordination of \( \text{NH}_3 \) on the catalyst, Eng et al [65] proposed that over zeolite catalysts, pairs of neighboring Brønsted acid sites are necessary for adsorption of \( \text{NH}_3 \); such that the adsorbed \( \text{NH}_3 \) molecules are close enough together that they can both bond with other reactant molecules. They also proposed that \( \text{NH}_3 \) must be adsorbed through the three hydrogen bonds in order to be reactive for SCR.

There can be many forms of intermediates when \( \text{NH}_3 \) is adsorbed on catalyst surfaces. Researchers [56] studied the activation form of \( \text{NH}_3 \) over Lewis acid sites and found that, after being coordinated on the catalyst surface, \( \text{NH}_3 \) undergoes hydrogen abstraction and gives rise either to -\( \text{NH}_2 \) amide species or to its dimeric \( \text{N}_2\text{H}_4 \) form, hydrazine. Other species tentatively identified as imide (\( \text{NH} \)), itroxyl (\( \text{HNO} \)), nitrogen anions (\( \text{N}_2^- \)), and azide anions (\( \text{N}_3^- \)) 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 \( \text{NH}_3 \) can be found in significant amounts on the catalyst surface. Lietti et al [67] proposed that over vanadium-based catalysts, \( \text{NH}_3 \) activation occurred via formation of a V-\( \text{NH}_2 \) 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 (\( E_d^{\circ} \)) was close to 25 kcal/mol, while \( E_a = 0 \) kcal/mol for \( \text{NH}_3 \) coverage varying from 0 to 80%, within a temperature range of 220 to 500ºC, suggesting a non-activated \( \text{NH}_3 \) 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, O₂ and NH₃ both affect catalytic activity. NH₃ is of course the reducing agent in the system. However, excess gaseous NH₃ appears to inhibit the SCR reaction by limiting access of the NOx species to adsorption sites within the zeolite [65]. Along this line, reported estimated kinetic order dependencies in NH₃ 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 NH₃ [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 O₂ is necessary for the standard SCR reaction. There has been some discrepancy for the order in O₂, ranging from 1.06 [65], 0.5 [70] to 0 – 0.13 [71]. Sjovall et al [7] studied the standard SCR reaction over Cu-ZSM-5 and found that O₂ 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, O₂ is necessary to regenerate Brønsted acid sites and V=O, which is supported by Tronconi et al [72]. They also found that at high O₂ partial pressures, the reaction rate is mainly determined by the concentration of Brønsted acid sites and NO partial pressure, whereas at low O₂ partial pressures, surface reoxidation is slow (discussed in the mechanistic aspects below) and the rate becomes dependent on the concentration of V⁵⁺=O groups.

Several factors affecting SCR reaction selectivity toward N₂ versus N₂O have been studied. The first factor is catalyst structure. Wachs et al [8] found that the selectivity toward N₂ formation over a V-based catalyst varies with the specific oxide support. For example, they found that among the supports tested, the performance was TiO₂ > Al₂O₃ > SiO₂. They also found that the selectivity toward N₂ decreased with the concentration of pairs of redox sites, too much of which will result in N₂O. Kieger et al [73] studied the standard SCR reaction over Cu-FAU and found that CuO aggregates lead to significant formation of N₂O. Delahay et al also studied N₂O formation during NOx SCR on Cu-FAU and found that besides CuO aggregates, N₂O could also form in the presence of NNN Cu ions, which may be similar to -HN-(CH₂)₂-
NH-(CH$_2$)$_2$-NH(CH$_2$)$_3$-Cu$^+$, located within the sodalite cages. N$_2$O 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$_2$O 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$_2$O was formed from two distinct reactions [78]. At relatively lower temperatures, beginning below 200ºC, N$_2$O is formed via equations (2.9) and (2.10). At temperatures above 400ºC, the oxidation of NH$_3$ by O$_2$ can produce N$_2$O by the following reaction (2.11).

$$4\text{NH}_3 + 4\text{O}_2 \rightarrow 2\text{N}_2\text{O} + 6\text{H}_2\text{O} \quad (2.11)$$

The third factor that affects N$_2$O formation is the ratio of NO$_2$ to NO as NOx. The thermal decomposition of ammonium nitrate is a standard method to produce N$_2$O in the laboratory [52]. A combination of low temperatures and high NO$_2$/NOx 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$_2$O 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 250ºC 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 NOx TPD results indicate negligible adsorption of NO$_2$ onto H-ZSM-5 at temperatures above 200ºC. 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 NH$_3$ involves a transfer, or a partial transfer, of hydrogen and reduced V-OH groups as a product. The O$_2$ regenerates the V$^{5+}$=O surface species. They proposed the following redox reaction sequence:

\[
\text{NH}_3 + V^{5+} - \text{OH} \leftrightarrow V^{5+} - \text{ONH}_4
\]

\[
V^{5+} - \text{ONH}_4 + V^{5+} = \text{O} \leftrightarrow V^{5+} - \text{ONH}_3 \text{H}^+ - \text{O} - V^{4+}
\]

\[
V^{5+} - \text{ONH}_3 \text{H}^+ - \text{O} - V^{4+} + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} + V^{5+} - \text{OH} + V^{4+} - \text{OH}^+
\]

\[
2V^{4+} - \text{OH}^+ \rightarrow \text{H}_2\text{O} + V^{3+} + V^{5+} = \text{O}
\]

\[
\text{O}_2 + 2V^{3+} \rightarrow 2V^{5+} = \text{O}
\]

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 NH$_3$ and reoxidized by O$_2$, as shown in Figure 2.1.

![Figure 2.1 Standard SCR redox scheme over V-based catalyst [72]](image)

Over zeolite-based catalysts, Eng et al [65] proposed that the main role of O$_2$ is to react with NO to form an active intermediate species, such as NO$_2$ 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 NH$_3$ onto neighboring acid sites and rearrangement of the NH$_4^+$ complexes to the 3H structure;
2. Reaction of adsorbed NH$_3$ with NO$_2$ to form an active complex, which reacts rapidly with NO or NO$_2$ to form N$_2$ or N$_2$O, respectively, leaving a residual complex; and
3. Decomposition of the residual complex to form additional N$_2$ and H$_2$O.

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 Cu$^{2+} \leftrightarrow$ Cu$^+$ redox mechanism, in which Cu$^{2+}$ is reduced to Cu$^+$ by NO + NH$_3$ and Cu$^+$ is oxidized to Cu$^{2+}$ by NO + O$_2$, with evolution of N$_2$ and H$_2$O.

### 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 NOx 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 NOx 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,

\[
\begin{align*}
2\text{NO}_2 + 2\text{NH}_3 & \rightarrow \text{N}_2 + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O} \quad (2.17) \\
\text{NO} + \text{NH}_4\text{NO}_3 & \rightarrow \text{NO}_2 + \text{N}_2 + 2\text{H}_2\text{O} \quad (2.18)
\end{align*}
\]

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.

![Fast SCR redox scheme over V-based catalyst](image.png)

**Figure 2.2 Fast SCR redox scheme over V-based catalyst [72]**
Colombo et al [185] recently proposed a detailed kinetic model of \( \text{NH}_3\)-NO/NO\(_2\) SCR reactions over a Cu-zeolite catalyst. The graphical abstract is shown in Figure 2.4. In this model, thirteen reactions are considered, including \( \text{NH}_3\), NO\(_2\) adsorption and desorption, nitrate decomposition, nitrite oxidation, and the reduction of nitrates and nitrites by \( \text{NH}_3\).
2.3.4 The role of NO$_2$ 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 NO$_2$ amount of NOx 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 NO$_2$ in SCR reactions.

Many groups agree that the effect of NO$_2$ in the V-based catalytic system is to serve as a more efficient oxidizing agent, in comparison to O$_2$, for the vanadium sites resulting in an increased reaction rate [52, 86-88]. Koebel et al [87] extensively investigated the reaction of NH$_3$ with NO/NO$_2$ on vanadia-based catalysts. The NO$_2$-enhanced reoxidation of the catalyst was demonstrated by in-situ Raman experiments over V$_2$O$_5$/TiO$_2$ and they found that the V$^{+4}$ species formed during the reduction of NO with NH$_3$ were reoxidized faster by NO$_2$ than by O$_2$, resulting in an increased reaction rate of the fast SCR reaction. Tronconi et al [72] investigated the redox mechanism governing the SCR of NO/NO$_2$ by NH$_3$ at low temperature using transient reactive experiments over a commercial V$_2$O$_5$/WO$_3$/TiO$_2$ catalyst. With temperature-programmed reaction runs, they found that NO$_2$ and HNO$_3$ were able to reoxidize the V catalyst at much lower temperature than O$_2$. At temperatures below 250ºC, NO$_2$ can significantly enhance the NO + NH$_3$ reactivity via the buildup of adsorbed nitrates, which they found could be decomposed above 250ºC. They proposed a unifying redox approach for the overall NO/NO$_2$–NH$_3$ SCR chemistry over V-based catalysts, in which vanadium sites are reduced by the reaction between NO and NH$_3$ and are reoxidized either by oxygen (standard SCR) or by nitrates (fast SCR), with the latter formed via NO$_2$ 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 NH$_4$NO$_3$ or related surface species as intermediates,

\[
2\text{NO}_2 + 2\text{NH}_3 \rightarrow \text{N}_2 + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O} \quad (2.19)
\]
\[
\text{NO} + \text{NH}_4\text{NO}_3 \rightarrow \text{NO}_2 + \text{N}_2 + 2\text{H}_2\text{O} \quad (2.20)
\]

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 NH$_3$. 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 NO$_2$ in SCR over Fe-ZSM-5 catalysys 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 NH$_3$ 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 NOx. 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 NOx 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 NOx some parasitic NH₃ oxidation is apparent at such temperatures. They suggested that NH₃ might be oxidized by NOx without reducing the latter to N₂ or N₂O. Girard et al investigated the influence of NH₃ to NOx ratio on SCR performance and found that at higher temperatures, more NH₃ is needed to improve NOx 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 300ºC, 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$_2$O.

The effect of P on Fe-zeolite catalyst performance was also studied by Silver et al [100], who found that P causes decreased NOx 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 100ºC to 500ºC. 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 350–400ºC, 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 Kucherov 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$_2$O, 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 (~3.8 Å) 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°C). Under fast SCR conditions, significant amounts of N$_2$O 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 NOx 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 NOx 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 intermediates 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 C\textsubscript{3}H\textsubscript{6} resulted in the occurrence of the fast SCR reaction combined with NO\textsubscript{2} SCR instead of pure NO\textsubscript{2} SCR. The reaction pathway change also decreased N\textsubscript{2}O formation significantly.

2.5  Kinetic modeling of the SCR DeNO\textsubscript{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 NH\textsubscript{3} adsorption, NO and NH\textsubscript{3} 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{equation}
\frac{-dC_{NH_3}}{dt} = k_1C_{NOCNH_3}/(1+K_{NOCNO})(1+K_{NH_3}C_{NH_3})
+ k_2C_{NH_3}/(1+k_{NH_3}C_{NH_3})
- k_3C_{Urea} - k_4C_{NHCOCH_2O}
\end{equation}

(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 NH\textsubscript{3} 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. \( \text{NH}_3 \) adsorption and desorption;
2. \( \text{NH}_3 \) oxidation;
3. NO oxidation;
4. standard SCR (NO + O\(_2\) + \( \text{NH}_3 \));
5. fast SCR (NO + NO\(_2\) + \( \text{NH}_3 \));
6. NO\(_2\) SCR (NO\(_2\) + \( \text{NH}_3 \)); and
7. \( \text{N}_2\text{O} \) 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 \( \text{NH}_3 \) molecules adsorbed per copper [132-133].

From their experiments, they found that the adsorption of NO\(_2\) was significantly less than \( \text{NH}_3 \) and they assumed that NO\(_2\) can only adsorb on S1a sites. They found that at temperatures as low as 30\(^\circ\)C, significant adsorption of \( \text{NH}_3 \) occurred, so they added S3 sites in the model to describe this phenomenon.

Water was found to reduce \( \text{NH}_3 \) 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. \( \text{NH}_3 \) inhibits the reaction likely by blocking the surface nitrates, i.e. high \( \text{NH}_3 \) 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 NOx conversions. Upon mixing with the hot exhaust gas, urea undergoes hydrolysis and thermal decomposition producing NH$_3$. 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 NH$_3$ will slip from the SCR catalyst. For example, sometimes more than enough urea will be injected into the system to increase deNOx efficiency and [136] excess NH$_3$ will be released into the environment. In order to minimize the amount of released NH$_3$, 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 NH$_3$, while the upper layer consists of an SCR catalyst to reduce the formed NOx with entering NH$_3$.

Early studies showed that when NOx is reduced over TWCs and LNT catalysts, NH$_3$ could form as a byproduct [28, 138]. Based on such findings, the concept of passive NH$_3$ SCR was recently proposed [139]. In this system, NH$_3$ is produced during rich operation, via reduction of the NOx over the TWC, or LNT. The produced NH$_3$ is then stored on the downstream SCR catalyst, and can be used as the reductant to reduce NOx during subsequent lean operation. So, for passive SCR systems, instead of supplying NH$_3$ via for example urea addition into the exhaust stream, NH$_3$ is produced on an upstream catalyst, and is then adsorbed on the SCR catalyst and used to reduce NOx to N$_2$. Chatterjee et al developed global kinetic models for the LNT + SCR catalysts, considering the accumulation of NOx and O$_2$ in the LNT and the adsorbed NH$_3$ in the SCR. The performance of this hybrid system was simulated with varying temperature and rich phase length, and their effects on NOx conversions and NH$_3$ yields were evaluated. The combined system provides better deNOx 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 NH$_3$ 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 NH$_3$ SCR systems for lean-burn spark-ignited, direct injection engines, whose key components include a close-coupled TWC and underfloor SCR catalyst. NH$_3$ is formed on the TWC with short pulses of rich engine operation and the NH$_3$ is then stored on the underfloor SCR catalyst. They found that NH$_3$ formation was highly sensitive to oxygen storage content in the TWC. The capability of SCR catalyst storage for NH$_3$ 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$_3$H$_6$ 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](image)

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.
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 180ºC.

With the entering gas mixture heated, there is the potential for NH₃ reactions along the upstream stainless steel (SS) tubing. To avoid this, NH₃ 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.
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.
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 NOx 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 NOx control strategy for both light-duty and heavy-duty applications. NH$_3$ 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 NH$_3$ storage capacity, which makes them promising for passive SCR.

Three types of NH$_3$-SCR reactions have been proposed (as introduced in Chapter 2); the standard, fast and NO$_2$-SCR reactions [88, 94, 159]. These descriptions are typically associated with the feed NO:NO$_2$ ratio. Standard SCR (4.1) refers to reaction between NH$_3$ and NO, with the participation of O$_2$; fast SCR (4.2) refers to the reaction between NH$_3$ and an equimolar ratio of NO and NO$_2$; and NO$_2$-SCR to N$_2$ (4.3) refers to reaction between NH$_3$ and NO$_2$ in the ratio of 4:3, with the formation of N$_2$ only. There are some other NO$_2$-SCR reactions, with a 1:1 consumption of NH$_3$ and NO$_2$, including the formation of NH$_3$ nitrate at low temperatures (4.4) and NO$_2$-SCR to N$_2$O (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 NO$_2$-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.

\[
\begin{align*}
4\text{NH}_3 + 4\text{NO} + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}; \\
2\text{NH}_3 + \text{NO} + \text{NO}_2 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}; \\
4\text{NH}_3 + 3\text{NO}_2 & \rightarrow 7/2\text{N}_2 + 6\text{H}_2\text{O}; \\
2\text{NH}_3 + 2\text{NO}_2 & \rightarrow \text{N}_2 + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}; \\
2\text{NH}_3 + 2\text{NO}_2 & \rightarrow \text{N}_2 + \text{N}_2\text{O} + 3\text{H}_2\text{O}; \\
2\text{NH}_3 + 3\text{O}_2 & \rightarrow \text{N}_2 + 3\text{H}_2\text{O}.
\end{align*}
\]

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 degreened 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 NOx (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 NOx (a) and NH₃ (b) conversions, as well as the N₂O concentration (c), at the reactor outlet as a function of NO₂/NOx ratio at different temperatures are shown in Figure 2. As shown in Figure 4.2 (a), NOx conversion is very sensitive to the NO₂/NOx ratio at temperatures between 250°C and 300°C, and a NO₂/NOx 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 NOx conversion on NO:NO₂ ratio decreases, and very high NOx conversion (generally around 90% or higher) can be achieved regardless of the NOx feed. At the highest temperature tested, 550°C, the NOx conversion actually decreased slightly when increasing the NO₂ ratio from 0.5 to 1. Based on the inlet NOX ratios, the different SCR reaction types have different dependencies on temperature. For the standard SCR (NO₂/NOx = 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/NOx = 0.5) conversion was consistently high, even at low temperatures, but decreased slightly at 500°C or higher. The conversion for NO₂-SCR (NO₂/NOx = 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 NOx 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 NOX conversion. Based on the N₂O outlet concentration profiles shown in Figure 2 (c), N₂O was only formed at NO₂/NOx > 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/NOx ratio increased from 0.75 to 1, which is due to the decreased NOx 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 NOx (a) and NH3 (b) conversions and N2O formation (c) as a function of NO2/NOx ratio at different temperatures. Feed gas composition: 600 ppm NOx, 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, NOx conversion monotonically increased as a function of catalyst length, in a near linear trend. At 300°C, NOx 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 NOx conversions are similar at 400 and 500°C, and higher than that at 300°C. The NOx 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 NOx and O₂ for NH₃. Compared with 300°C, the higher NOx conversions at 400 and 500°C indicate increased reactivity between the NH₃ and NOx relative to O₂. So, although the oxidation of NH₃ by O₂ is of course also increased with increasing temperature (shown below), the reactivity of NOx with NH₃ is increased to a greater extent.

![Graph showing NOx conversion vs. position at different temperatures](image URL)
Figure 4.3 Spatial NOx conversion (a), NOx (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 NH₃ conversion during its oxidation by O₂ at different temperatures. Feed gas composition: 600 ppm NH₃, 2.4% H₂O, 5% CO₂, 8% O₂, balance N₂; 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 NH₃ and O₂ 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 NH₃ was oxidized
by O2. However, the general increase in NOx 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 NOx conversion is shown in Figure 4.5(b). NO and NH3 concentrations were both fixed at 600 ppm. NOx conversion increased monotonically with increasing O2 concentration at 200 and 250°C. Since the NOx 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 NOx conversion close to zero.

The results of the effect of NH3 concentration (from 150 to 1000 ppm) on NOx 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 NOx 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 NOx 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 NOx reduction decreases with increasing NH3 giving rise to an observed NH3 inhibition effect on NOx 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 NOx 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 NOx conversion as a function of (a) NO feed concentration (NH$_3$ = 600ppm, O$_2$ = 8%), (b) O$_2$ concentration (NH$_3$ = NO = 600 ppm), and (c) NH$_3$ concentration (NO = 600ppm, O$_2$ = 8%) at different temperatures; the balance gas composition was: 2.4% H$_2$O, 5% CO$_2$, balance N$_2$; GHSV = 28,000 h$^{-1}$.

For simplicity, the kinetics of the standard SCR reaction are expressed as a power-law rate equation: $r = k[NO]^{\alpha}[O_2]^{\beta}[NH_3]^{\gamma}$. 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 O$_2$ 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 NH$_3$ 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 NH$_3$ 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 O$_2$, 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 NH$_3$ is due to the strong adsorption of NH$_3$ 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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>NO</th>
<th>O₂</th>
<th>NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO oxidation</td>
<td>1.00 (0.99)</td>
<td>0.57 (0.99)</td>
<td>n/a</td>
</tr>
<tr>
<td>standard SCR</td>
<td>0.97 (0.99)</td>
<td>0.56 (0.99)</td>
<td>-0.43 (0.99)</td>
</tr>
</tbody>
</table>

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 NOx 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 NOx 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, NOx and NH₃ consumption was significant, with conversions higher than 50%. Therefore, the NH₃ concentration is sensitive to the input NOx. Higher NOx 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 NOx conversion was observed as the NOx 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% O\textsubscript{2}, 2.4% H\textsubscript{2}O, 5% CO\textsubscript{2}, balance N\textsubscript{2}; GHSV = 28,000 h\textsuperscript{-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\degree C, and then decreased from 400 to 500\degree C. The reason that the highest NO conversion being achieved at 400\degree C is due to NO oxidation being kinetically limited at lower temperatures and thermodynamically limited at higher temperatures. Spatially-resolved NO\textsubscript{2} concentrations along the catalyst at different temperatures were measured, and the results are shown in Figure 6. The NO\textsubscript{2} 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 NH₃ reacting with NOₓ, via the fast SCR reaction, rather than with O₂ 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 NO₂ concentrations at 1.2 cm, as shown in Figure 4.8, were also quite small. Therefore, these results consistently suggest that NO reduction by NH₃ is closely related to NO oxidation.

![Figure 4.7 Spatial NO₂ concentration profiles during NO oxidation at different temperatures. Feed gas composition: 600 ppm NO, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.](image-url)
Figure 4.8 Spatial NOx conversion (a), NOx 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. NH₃, 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 NH₃ 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 NH₃ oxidation by O₂. 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 O₂ for reductant NH₃, 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 NO₂. The spatially resolved gas concentration results for the fast SCR reaction (NO₂/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 NH₃ 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 NH₃ oxidation by O₂ at high temperature, which is confirmed by the NOx and NH₃ 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 NO₂ and NH₃ can occur without catalyst in the presence of H₂O. This reaction can be confirmed by the formation of white powder NH₄NO₃ inside the front tube if NO₂, NH₃ and H₂O were introduced at the same time, for long enough time periods.

4.3.4 Spatial resolution of NO₂-SCR

The spatially-resolved gas concentration results for NO₂-SCR at different temperatures are shown in Figure 4.9. Compared with the other two SCR reactions, as shown in Figure 4.2 (a), NO₂-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 NO₂ and NH₃ does not occur solely through reaction (4.3), namely NO₂-SCR to N₂, where the theoretical maximum NOx conversion is only 75%. It is likely that the NO₂-NH₃ reaction also occurs through NO₂-SCR to N₂O with equimolar consumption of NH₃ and NO₂.
Significant N$_2$O formation supports this path. As shown in Figure 4.2(c), the N$_2$O outlet concentration decreases with increasing temperature above 250°C.

N$_2$O concentrations as a function of catalyst position are plotted in Figure 4.9 (b). At 300 and 400°C, N$_2$O was readily formed, and then kept relatively constant. However, at 500°C, the N$_2$O concentration first increased to about 60 ppm in the front 0.6 cm, but then slowly decreased, indicating that the N$_2$O formed in the front of the catalyst decomposes at the back. This is consistent with previous results showing that N$_2$O starts to decompose on Fe-ZSM-5 at 450°C [94]. On this basis, N$_2$O decomposition at high temperatures is at least one of the reasons for the observed decrease in N$_2$O concentration with increasing temperature.
Figure 4.9 Spatial NOx conversion (a), N\textsubscript{2}O concentration (b) profiles along the catalyst at different temperatures during NO\textsubscript{2}-SCR. Feed gas composition: 600 ppm NO\textsubscript{2}, 600 ppm NH\textsubscript{3}, 8\% O\textsubscript{2}, 2.4\% H\textsubscript{2}O, 5\% CO\textsubscript{2}, balance N\textsubscript{2}; GHSV = 28,000 h\textsuperscript{-1}.

Another contributing factor for decreased N\textsubscript{2}O formation with increasing temperature could be an increase in the NO\textsubscript{2}-SCR to N\textsubscript{2} relative to the NO\textsubscript{2}-SCR to N\textsubscript{2}O reaction. The extent of NO\textsubscript{2}-SCR to N\textsubscript{2} can be inferred by comparing NOx conversions at 550°C. Based on the data shown in Figure 5.2, NOx conversion with pure NO\textsubscript{2} as the NOx source at 550°C, around 80\%, is lower than that observed under standard SCR conditions, where with pure NO as the NOx source, around 90\% was achieved. It would be expected that less NH\textsubscript{3} is oxidized by O\textsubscript{2} using NO\textsubscript{2} as the NOx source due to its higher reactivity, and therefore more NH\textsubscript{3} reacts with NO\textsubscript{2}, compared with NO in the standard SCR reaction. This therefore suggests that NO\textsubscript{2}-SCR to N\textsubscript{2} at 550°C is the more dominant pathway, with the 80\% conversion close to the theoretical 75\% value if an equimolar amount of NO\textsubscript{2} and NH\textsubscript{3} is introduced. Furthermore, at temperatures above 450°C, with increasing relative NO\textsubscript{2} (NO\textsubscript{2}/NOx > 0.5) in the feed gas, the NOx
conversion tends to decrease, indicating that increased NO2-SCR to N2 occurs, which decreases the overall NOx 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 NOx 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.

\[ \text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3 \] (4.7)

\[ 4\text{HNO}_3 \rightarrow 4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \] (4.8)

\[ 4\text{NH}_3 + 4\text{NO}_2 \rightarrow 4\text{N}_2 + \text{O}_2 + 6\text{H}_2\text{O} \] (4.9)

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 NOx 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 NH₄NO₃ to NH₃ and HNO₃, then HNO₃ to NO₂ and O₂, and possibly NO₂ decomposition to NO and O₂, contribute to decreased N₂O formation.

### 4.3.5 Spatial resolution of SCR with different NO₂ feed concentrations

In real application, depending on driving conditions and the upstream DOC’s performance, NO₂ concentrations will fluctuate. In order to figure out the reaction patterns and the length of catalyst used for different NO₂ levels, NOx conversion with different NO₂/NOx 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 NO₂ < fast SCR. The catalyst lengths used to achieve 80% NOx 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 NOx conversion values for these three reactions are 35%, 74% and 94%, respectively.

![Figure 4.10 Spatial NOx conversion along the catalyst at 300°C with different NO₂ feed concentrations. Feed gas composition: 600 ppm NOx (NO₂: 0 – 600 ppm), 600 ppm NH₃, 8% O₂, 2.4% H₂O, 5% CO₂, balance N₂; GHSV = 28,000 h⁻¹.](image)

For the case with 450 ppm NO and 150 ppm NO₂, the reaction occurs very fast in the front 0.4 cm, higher than SCR with pure NO₂, and then the reaction slows and ceases at about 2.0 cm. The NOx, NH₃ and NO₂
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 NOₓ 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 NOₓ, 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 NOx(solid), NH\(_3\)(hollow) and NO\(_2\)(cross) concentration profiles at 150°C (black) and 300°C (red); and (b) NH\(_3\), NO and NO\(_2\) consumption profiles along the catalyst at 300°C. Feed gas composition: 450 ppm NO, 150 ppm NO\(_2\), 600 ppm NH\(_3\), 8% O\(_2\), 2.4% H\(_2\)O, 5% CO\(_2\), balance N\(_2\); GHSV = 28,000 h\(^{-1}\).

Different behaviour was observed for the case with 150 ppm NO and 450 ppm NO\(_2\). The NOx and NH\(_3\) 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 NH\(_3\) and NO\(_2\) occurs by the front of the catalyst, which consumes about 90 ppm of both NH\(_3\) and NO\(_2\), as shown in Figure 4.12(a), since only 510 ppm NOx and NH\(_3\) are observed at the zero position. From Figure 4.12(b), more NO\(_2\) is consumed than NO, and increasing N\(_2\)O production (data not shown) was observed in the front 0.8 cm,
where NO is also totally consumed. This demonstrates that NO\textsubscript{2}-SCR and the fast SCR reactions proceed in parallel.

Figure 4.12 (a) Spatially-resolved NO\textsubscript{x}, NH\textsubscript{3} and NO and NO\textsubscript{2} concentration profiles at 300\textdegree C; and (b) NH\textsubscript{3}, NO and NO\textsubscript{2} consumption profiles along the catalyst. Feed gas composition: 150 ppm NO, 450 ppm NO\textsubscript{2}, 600 ppm NH\textsubscript{3}, 8\%O\textsubscript{2}, 2.4\% H\textsubscript{2}O, 5\% CO\textsubscript{2}, balance N\textsubscript{2}; GHSV = 28,000 h\textsuperscript{-1}. 

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The different reaction patterns, in series or in parallel, with respect to different NO\textsubscript{2} levels, can be rationalized by the relative rates between fast SCR, standard SCR and SCR with pure NO\textsubscript{2}. In summary, the reaction patterns at 300°C are determined by the NO\textsubscript{2} ratio in the feed gas. If NO\textsubscript{2}/NO\textsubscript{x} < 0.5, as in the case with 450 ppm NO and 150 ppm NO\textsubscript{2}, the reactions proceed in series, namely first the fast SCR reaction followed by standard SCR. If NO\textsubscript{2}/NO\textsubscript{x} > 0.5, as in the case with 150 ppm NO and 450 ppm NO\textsubscript{2}, the reactions proceed in parallel, with fast SCR and NO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{3} supply since part of the NH\textsubscript{3} is oxidized by O\textsubscript{2} and equimolar amounts of NH\textsubscript{3} and NO were added. Increasing the temperature past 300°C results in more significant NO\textsubscript{x} reduction since NO oxidation significantly increases, which also increases the selectivity of NH\textsubscript{3} reacting with NO\textsubscript{x} rather than O\textsubscript{2}.

NO\textsubscript{2}-SCR with equimolar NH\textsubscript{3} and NO\textsubscript{2} feed results in significant N\textsubscript{2}O production, and N\textsubscript{2}O formation tends to decrease with increasing temperature above 250°C. At temperatures between 300 to 400°C, besides the N\textsubscript{2}O formation route, other reactions contribute to decreased N\textsubscript{2}O formation, including the decomposition of NH\textsubscript{3}NO\textsubscript{3} into HNO\textsubscript{3} then to NO\textsubscript{2} and O\textsubscript{2}, and/or NO\textsubscript{2} decomposition into NO and O\textsubscript{2}. At high temperatures, both the enhanced NO\textsubscript{2}-SCR to N\textsubscript{2} and N\textsubscript{2}O decomposition at the back part of the catalyst contribute to decreased N\textsubscript{2}O formation as well.

Different reaction patterns were observed for unbalanced NO:NO\textsubscript{2} ratios (≠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\textsubscript{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.
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 NOx 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 Kucherov 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 NOx 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 was 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\textsubscript{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 170ºC 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\textsubscript{2} and NH\textsubscript{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\textsubscript{x} (NO+NO\textsubscript{2}), 400 ppm NH\textsubscript{3}, 10\% O\textsubscript{2}, 5\% H\textsubscript{2}O, 7\% CO\textsubscript{2} and balance N\textsubscript{2}, and the total gas flow rate was 4.8 L/min, corresponding to a gas hourly space velocity (GHSV) of 48,000 h\textsuperscript{-1}. For NH\textsubscript{3} oxidation tests, the NH\textsubscript{3} inlet concentration was 360 ppm, while O\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2} were the same as above, and the GHSV was 48,000 h\textsuperscript{-1}. For NO oxidation, the NO inlet concentration was 200 ppm, while O\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2} levels were the same as above, and the GHSV was 30,000 h\textsuperscript{-1}. For NH\textsubscript{3} adsorption, the NH\textsubscript{3} inlet concentration was 200 ppm, while O\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2} were the same as above, and the GHSV was 30,000 h\textsuperscript{-1}. The quantity of adsorbed NH\textsubscript{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 NO\textsubscript{2} ratios, and NH\textsubscript{3} 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\textsubscript{x} and NH\textsubscript{3}, and NH\textsubscript{3} oxidation results, obtained either via the spatial resolution technique when measuring at 1.8 cm or through the normal method, were approximately the same. As an example, the NO conversion results as a function of temperature obtained during the two types of tests for the medially aged catalyst are shown in Figure 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\textsubscript{x} and NH\textsubscript{3} conversions observed during standard SCR, fast SCR, and NH\textsubscript{3} oxidation reaction tests were higher than those obtained during the normal tests, with the NO conversion as a function of temperature during standard SCR as an example, shown in Figure 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, O\(_2\) = 10\%, H\(_2\)O = 5\%, CO\(_2\) = 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, O\(_2\) = 10\%, H\(_2\)O = 5\%, CO\(_2\) = 7\%.

Based on the above results, the homogeneity of catalyst aging was evaluated for the three aged catalyst samples. Standard SCR, fast SCR and NH\(_3\) 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 NOx 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 NOx conversions at 250°C in channels located at different radial positions in the highly aged catalyst. GHSV = 48,000 h\(^{-1}\), inlet concentrations NH\(_3\) = 400 ppm, NO = 200 ppm, NO\(_2\) = 200 ppm, O\(_2\) = 10%, H\(_2\)O = 5%, CO\(_2\) = 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 NOx 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 h$^{-1}$, inlet concentrations NO = 200 ppm, O$_2$ = 10%, H$_2$O = 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 300ºC, 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 NO₂ production at high temperature occurring in the outlet portion of the catalyst as a function of NH₃ 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 NO₂ noted, due to the fact that a very small fraction of the NO was oxidized via reaction with O₂ prior to the catalyst inlet. The NO₂ concentration dropped along the catalyst length due to the fast SCR reaction. However, as the NH₃ concentration decreased to around 50 ppm, NO₂ 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, NO₂ production began earlier although the concentration of NH₃ was still quite high, suggesting a balance between NO oxidation and SCR at limited NH₃ concentrations.

![Figure 5.6 NH₃ and NO₂ concentration profiles along the lightly aged catalyst. GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NO = 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.](image)

5.3.3.2 Hydrothermal aging effects on NO and NH₃ conversion for the standard SCR reaction

The effects of catalyst hydrothermal aging on NO and NH₃ 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 NH₃ 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 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,

\[ 4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \]  \hspace{1cm} (5.1)
Therefore, the quantity of NO consumed is the quantity of NH$_3$ oxidized by NO, and the difference between total NH$_3$ consumption and NO consumption is the quantity of NH$_3$ overconsumption, which under steady-state conditions represents NH$_3$ oxidation by oxygen. With the spatial resolution technique, the quantities of NH$_3$ and NO consumed for each section were calculated. The selectivity of NH$_3$ oxidation by O$_2$ over NH$_3$ oxidation by NO in each section was calculated as follows:

$$S = \frac{(\text{NH}_3 \text{ consumed} - \text{NO consumed})}{\text{NO consumed}}$$

The selectivity data are plotted in Figure 5.9. As shown in Figure 5.7, NH$_3$ overconsumption was not evident at temperatures below 300ºC. At temperatures above 435ºC, the significance of NH$_3$ 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 516ºC, NH$_3$ oxidation by O$_2$ 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 oxocatic Cu species in Cu-FAU for NH$_3$ oxidation by oxygen. The results reported here suggest that there are CuO particles present in the highly aged Cu-zeolite catalyst.

![Figure 5.9](image_url)

**Figure 5.9** Effects of temperature and catalyst hydrothermal aging on the selectivity of NH$_3$ oxidation by O$_2$ over NH$_3$ oxidation by NO. GHSV = 48,000 h$^{-1}$, inlet concentrations NH$_3$ = 400 ppm, NO = 400 ppm, O$_2$ = 10%, H$_2$O = 5%, CO$_2$ = 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 NO\textsubscript{2} in the system was decomposed into NO, driven by thermodynamic equilibrium constraints at high temperature. And as will be shown later, NO\textsubscript{2} in an equimolar NO/NO\textsubscript{2} 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 NH\textsubscript{3} conversion for all three aged catalysts (data not shown) increased monotonically with temperature while NOx conversion dropped at high temperatures, demonstrating that NH\textsubscript{3} 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\textsuperscript{-1}, inlet concentrations NO = 200 ppm, NO\textsubscript{2}= 200 ppm, O\textsubscript{2} = 10%, H\textsubscript{2}O = 5%, CO\textsubscript{2} = 7%.

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

The effects of catalyst hydrothermal aging on NOx 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 NOx 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 NOx 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 NOx 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%.](image)

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, NOx 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 NOx 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 NO\textsubscript{2} decomposition as a function of temperature and catalyst length in different channels over the highly aged Cu-zeolite catalyst. GHSV = 48,000 h\textsuperscript{-1}, inlet concentrations NO = 200 ppm, NO\textsubscript{2} = 200 ppm, O\textsubscript{2} = 10%, H\textsubscript{2}O = 5%, CO\textsubscript{2} = 7%.

5.3.5 Spatially-resolved NH\textsubscript{3} oxidation

5.3.5.1 Temperature effect on concentration/conversion profiles

As discussed, the consumption of NH\textsubscript{3} by oxygen instead of being used in the SCR reactions is a critical negative impact on the overall performance. NH\textsubscript{3} oxidation conversions are shown in Figure 5.13. NH\textsubscript{3} oxidation occurred at all temperatures tested. For temperatures below 400\degree C, NH\textsubscript{3} oxidation conversion increased almost linearly along the catalyst length. At temperatures higher than 500\degree C, NH\textsubscript{3} was consumed by oxygen very quickly, suggesting that NH\textsubscript{3} overconsumption will be a very strong competitor with NH\textsubscript{3} SCR at high temperatures. Also, as shown in the figure, at 615\degree C nearly 40 ppm NO\textsubscript{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 NOx generation from NH₃ oxidation

The effect of catalyst hydrothermal aging on NOx 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 NOx 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 NOx, while the medially aged catalyst produced the least.
Figure 5.14 Hydrothermal aging impact on NOx output during NH$_3$ oxidation as a function of temperature and catalyst position. GHSV = 48,000 h$^{-1}$, inlet concentrations NH$_3$ = 360 ppm, O$_2$ = 10%, H$_2$O = 5%, CO$_2$ = 7%.

The NH$_3$ conversions as a function of temperature and catalyst length during NH$_3$ oxidation are plotted in Figure 5.15. NH$_3$ conversion obviously depends on reaction temperature. The lightly aged catalyst resulted in the highest NH$_3$ conversion rates from 300 to 620ºC. The data plotted in Figure 5.15(a) show that between 300 and 350 ºC, NH$_3$ conversion rates decreased monotonically with hydrothermal aging extent. But at higher temperatures, Figure 5.15(b), higher NH$_3$ 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 NOx through NH$_3$ oxidation at high temperatures. When there is NOx in the system, SCR can of course occur. The consumption of NH$_3$ can therefore include both oxidation and SCR. Therefore, the highly aged catalyst is more active than the medially aged catalyst for NH$_3$ conversion due to its higher capability in producing NOx at high temperatures.
Figure 5.15(a) Catalyst hydrothermal aging effect on NH₃ conversion in NH₃ oxidation as a function of temperature (300 °C – 350 °C). GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 360 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.

Figure 5.15(b) Catalyst hydrothermal aging effect on NH₃ conversion in NH₃ oxidation as a function of temperature (400°C – 620°C). GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 360 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.
5.3.6 Spatially-resolved effect of NO: NO\textsubscript{2} ratio

5.3.6.1 Effect of NO: NO\textsubscript{2} ratio on SCR

In order to understand the effect of NO to NO\textsubscript{2} ratio on NH\textsubscript{3} SCR performance, NO: NO\textsubscript{2} ratios were varied, from 400 ppm NO: 0 ppm NO\textsubscript{2} to 0 ppm NO: 400 ppm NO\textsubscript{2}, at 200\(^\circ\)C for the three differently aged Cu-zeolite catalysts. The NO\textsubscript{x} conversion results as a function of NO: NO\textsubscript{2} and catalyst position for the medially aged catalyst are shown in Figure 5.16. The NO\textsubscript{x} conversion was highest, reaching 80\%, as expected, when the NO: NO\textsubscript{2} 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 NO\textsubscript{2} SCR. The NO\textsubscript{x} conversions for NO: NO\textsubscript{2} ratios around 2:1 and 3:5 are very close. The main reason for this similarity in conversion is that at 200\(^\circ\)C, the fast SCR reaction is the dominant reaction, leading to 2/3 of the entering NO\textsubscript{x} being consumed.

![Figure 5.16](image-url)

Figure 5.16 NO\textsubscript{x} conversion profiles as a function of catalyst length and NO: NO\textsubscript{2} concentration over the medially aged Cu-zeolite catalyst. 
GHSV = 48,000 h\textsuperscript{-1}, inlet concentrations NH\textsubscript{3} = 400 ppm, NO\textsubscript{x} = 400 ppm, O\textsubscript{2} = 10\%, H\textsubscript{2}O = 5\%, CO\textsubscript{2} = 7\%.
5.3.6.2 Reaction sequence

When both NO and NO\textsubscript{2} are part of the inlet gases, in theory all three SCR reactions can occur. To determine which are occurring, the amounts of NO and NO\textsubscript{2} consumed along the catalyst length need to be measured and compared. The reduction in NO and NO\textsubscript{2} concentrations over unit lengths of catalyst for the lightly aged catalyst, when the inlet concentrations of NO and NO\textsubscript{2} were 200 ppm each, are shown in Figure 5.17. At 182ºC, the consumption of NO\textsubscript{2} 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 NH\textsubscript{3} and NO\textsubscript{2} occurs simultaneously. At 297ºC, the consumption of NO and NO\textsubscript{2} along the catalyst are the same, demonstrating that fast SCR is the only reaction occurring. At 516ºC, more NO\textsubscript{2} 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 NO\textsubscript{2} consumption is likely associated with NO\textsubscript{2} decomposition to NO, and NO\textsubscript{2} SCR.

![Figure 5.17 Change of NO and NO\textsubscript{2} consumption over unit lengths of catalyst along the lightly aged catalyst as a function of reaction temperature (inlet NOx concentration ratio NO:NO\textsubscript{2} = 200:200). GHSV = 48,000 h\textsuperscript{-1}, inlet concentrations NH\textsubscript{3} = 400 ppm, NOx = 400 ppm, O\textsubscript{2} = 10\%, H\textsubscript{2}O = 5\%, CO\textsubscript{2} = 7\%.]
The consumption of NO and NO\textsubscript{2} along the lightly aged catalyst at two different temperatures, with inlet NO and NO\textsubscript{2} concentrations of 262 and 126 ppm, respectively, are shown in Figure 5.18. At 193\textdegreeC, in the first 0.5 cm section of the catalyst, the fast SCR reaction dominates and a small amount of reaction between NH\textsubscript{3} and NO\textsubscript{2} is observed. As the NO\textsubscript{2} concentration drops, the standard SCR reaction becomes more significant, although the fast SCR reaction obviously still occurs. At 553\textdegreeC, 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 NO\textsubscript{2}.

![Figure 5.18](image)

Figure 5.18 Change in NO and NO\textsubscript{2} consumption per unit length of catalyst along the lightly aged catalyst as a function of reaction temperature (inlet NOx concentration ratio NO:NO\textsubscript{2} = 262:126). GHSV = 48,000 h\textsuperscript{-1}, inlet concentrations NH\textsubscript{3} = 400 ppm, NOx = 388 ppm, O\textsubscript{2} = 10\%, H\textsubscript{2}O = 5\%, CO\textsubscript{2} = 7\%.

**5.3.6.3 Effect of hydrothermal aging on NOx reduction with varying NO:NO\textsubscript{2} ratio**

The effects of hydrothermal aging on fast SCR and standard SCR were discussed above. In this section, the other three NO:NO\textsubscript{2} 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:NO\textsubscript{2} ratio. The effect of hydrothermal aging on NO and NO\textsubscript{2} conversions at 200\textdegreeC are shown in Figure 5.20, and the NO
and NO₂ conversions decreased almost in parallel, suggesting that the aging effects on the SCR reactions with various NO:NO₂ ratios are not differentiated at 200°C.

Figure 5.19 Catalyst hydrothermal aging effect on NOx conversion for various NO: NO₂ ratios (200°C). GHSV = 48,000 h⁻¹, inlet concentrations NH₃ = 400 ppm, NOx ~ 400 ppm, O₂ = 10%, H₂O = 5%, CO₂ = 7%.
Figure 5.20 Hydrothermal aging effect on NO and NO\textsubscript{2} conversions for various NO:NO\textsubscript{2} ratios (200°C). GHSV = 48,000 h\textsuperscript{-1}, inlet concentrations NH\textsubscript{3} = 400 ppm, NOx \sim 400 ppm, O\textsubscript{2} = 10%, H\textsubscript{2}O = 5%, CO\textsubscript{2} = 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, NH\textsubscript{3} conversions changed monotonically with temperature and catalyst length. NH\textsubscript{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\textsubscript{3}. Therefore, for standard SCR and fast SCR, NOx conversion attained its maximum at 300°C. In fast and standard SCR, hydrothermal aging decreased reaction rates for SCR and NH\textsubscript{3} overconsumption simultaneously. Selectivity to NH\textsubscript{3} 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 NH\textsubscript{3} concentrations. NO conversion under standard SCR conditions was more heavily
affected by hydrothermal aging than NOx 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 NOx produced during NH₃ oxidation. However, the highly aged catalyst produced a higher proportion of NOx. At 200°C, hydrothermal aging did not show appreciable effects on the SCR extent with various NO:NO₂ ratios.
Chapter 6 NH₃ Pulsing Adsorption and SCR Reactions over a Cu-CHA SCR Catalyst

6.1 Introduction

Nitrogen oxides (NOx) 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 NOx emissions. NOx 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 NOx from automotive exhaust [188], where expensive platinum group metals (PGM) are the active components, over which NOx is reduced by CO or hydrocarbons. For diesel engines, lean NOx traps (LNT) and selective catalytic reduction (SCR) catalysts are two approaches in eliminating NOx. This paper focuses on SCR, where NOx is reduced on a catalyst with NH₃ as the reductant.

Early studies showed that when NOx 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 NOx 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 NOx 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 NOx 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\textsubscript{2}, in particular low N\textsubscript{2}O 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\textsubscript{2}O.

### 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\textsubscript{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.](image)

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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 NOx/O₂ and NH₃ prior to the catalyst on the upstream stainless steel tubing, they were introduced separately into the reactor. NH₃ and NOx/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 NOx/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/NOx 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/NOx 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\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2} to purge the system. The “cleanness” of the catalyst was inspected by monitoring the gas phase composition. When the concentrations of NH\textsubscript{3}, NO and NO\textsubscript{2} along the length of catalyst in the gas phase were known, the quantity of NH\textsubscript{3} adsorbed on the catalyst surface and the quantities of NO and/or NO\textsubscript{2} consumed due to the SCR reactions could be calculated. And vice versa, knowing how much NO or NO\textsubscript{2} was consumed along the length of catalyst allows determination of how much NH\textsubscript{3} was distributed along the length of the catalyst. Ultimately this demonstrates where the NH\textsubscript{3} is adsorbed with changes in pulse parameters, but also if and to what extent NH\textsubscript{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\textsubscript{3} on the catalyst is calculated based on the change of NH\textsubscript{3} concentration in the gas phase and the gas volume flow rate. The concentration of NH\textsubscript{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\textsubscript{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\textsubscript{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 though 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\textsubscript{2} concentration. The inlet concentration of CO\textsubscript{2} was kept the same and there is no formation or consumption of CO\textsubscript{2} in the reaction or system. Therefore, the CO\textsubscript{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\textsubscript{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 1.65μmol/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 NH₃ adsorption profiles as a function of NH₃ exposure time; conditions: 250°C; lightly aged catalyst; NH₃ inlet concentration = 419 ppm.

To evaluate the effect of NH₃ inlet concentration versus pulse time (for the same ultimate amount of NH₃ added), NH₃ inlet concentrations and pulse times were varied accordingly, and the data are shown in Figure 6.4. For a shorter pulse time, the NH₃ inlet concentration was higher; for a longer pulse time, a lower NH₃ 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 NH₃ inlet concentration is proportional to the quantity of introduced NH₃, with a ratio of 3:2:1 for the tests run. For the largest amount of NH₃ introduced, the NH₃ adsorption profiles were very similar. However, for the two with lesser amounts of NH₃ introduced, there were differences evident between the NH₃ adsorption profiles. In these with less NH₃ input, the adsorption profiles associated with the higher NH₃ inlet concentration and shorter pulsing time were steeper than the adsorption profiles associated with lower NH₃ inlet concentration and longer pulse time. These results indicate that the extent of NH₃ adsorption is a concentration driven process toward the beginning of adsorption, i.e. away from saturation. Of course,
with a higher NH₃ inlet concentration, there will be a higher adsorption rate. On the other hand, the driving force also depends on the surface NH₃ concentration, where a maximum exists. At the beginning of the NH₃ pulsing adsorption process, the catalyst was clean and there was no NH₃ on the solid surface and therefore, the NH₃ adsorption rate is purely dependent on the NH₃ inlet concentration. And of course as the surface concentration increases, the driving force for adsorption decreases.

Figure 6.4 Effects of NH₃ concentration and pulsing time on NH₃ 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 NH₃ adsorption at the onset of the dose when a larger inlet NH₃ 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 NH₃ adsorption profiles, comparison tests were done on the lightly and highly aged catalysts for two sets of inlet conditions at 250°C. NH₃ adsorption profiles are shown in Figure 6.5. Compared with the NH₃ 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.

![Graph](image)

Figure 6.5 Effect of aging on NH$_3$ adsorption profiles; conditions: 250°C; pulsing time in seconds × NH$_3$ inlet concentration in ppm: a1:20×1150 with the lightly aged catalyst; a2: 20×1150 with the highly aged catalyst; b1:60×419 with the lightly aged catalyst; b2: 60×419 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 1.5μmol/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 NH₃ at the back of the catalyst, for conditions that do not approach full saturation.

![Figure 6.6 Effect of temperature on NH₃ adsorption profiles; conditions: lightly aged catalyst; NH₃ inlet concentration: 419 ppm.](image)

### 6.3.2 NH₃ 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 NOx reaching the downstream catalyst. Of key interest is NH₃ migration along the SCR catalyst prior to, or during NOx exposure. NH₃ adsorption and desorption can occur along the monolith, analogous to what occurs in a gas chromatograph column. And, even with NOx present, NH₃ migration may still be occurring as NOx is consumed upstream. The differences between the NOx consumption profiles and NH₃ pulse adsorption profiles can be used to evaluate NH₃ migration within the time gap between the NH₃ pulse ending and the SCR reaction beginning.

The fast SCR reaction was used to characterize NH₃ migration. Factors such as time gap, temperature, and catalyst aging on NH₃ migration were investigated. Assuming the SCR reactions follow standard and/or fast SCR reaction mechanisms [88, 94, 158], from the consumption of NOx the NH₃ 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 adsorptions 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 NH₃ from the front part of the catalyst, thus decreasing the required amount of rich time to generate NH₃. Another conclusion that can be drawn from these observations is that both weakly and strongly adsorbed NH₃ can readily react with NO or NOₓ.

Regarding the effect of catalyst aging on NH₃ migration and loss, similar experiments were done with the lightly aged catalyst at 250°C, with time gaps of 10 and 70 seconds. The NOₓ consumptions per unit length of catalyst over the lightly and highly aged catalysts were measured (but not shown here for brevity). The conditions for NH₃ and NOₓ pulsing were the same as those described in Figure 6.7(a). As discussed above, aging results in less NH₃ adsorption and thus the adsorption profiles were more even along the length of catalyst. And as would be expected, the NOₓ consumption profiles for the highly aged catalyst were also flatter.

Figure 6.7(a) NH₃ migration after adsorption: effect of time gap: conditions: 250°C; highly aged catalyst; NH₃ inlet concentration: 1150 ppm; NH₃ pulsing time: 20 seconds; NOₓ inlet concentration: 416 ppm; NO:NO₂ = 1:1; NOₓ 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; NOx inlet concentration: 416 ppm; NO:NO$_2$ = 1:1; NOx 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 NOx 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; NOx inlet concentration: 416 ppm; NO:NO$_2$ = 1:1; NOx 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 NOx 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; NOx inlet concentration: 416 ppm; NO: NO$_2$ = 1:1; NOx 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. NOx consumption data along the catalyst are shown in Figure 6.10.
Figure 6.10 Comparison between NH$_3$ adsorption profiles and NOx consumption profiles under fast SCR reaction conditions; test conditions: 250°C; lightly aged catalyst; NOx inlet concentration during the NOx pulse: 416 ppm; NO: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 NOx 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 NOx 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 NOx pulse.

For the same reasons discussed above, the data from all three groups of comparisons showed that NOx consumption profiles along the length of catalyst were flatter than their corresponding NH$_3$ pulsing adsorption profiles. In the front part of the catalyst, NOx consumption quantities were less than the
amount of NH$_3$ adsorbed during the NH$_3$ pulse; while in the back of the catalyst, NOx 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 NOx 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 NOx 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 NOx consumption over a unit length of catalyst were similar. The data in Figure 6.11 show the integral NO/NOx 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 NOx 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; NOx inlet concentration: 416 ppm; time gap between NH₃ pulsing adsorption and NO or NOx 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 NOx consumption did show a dependence on the relative ratio of NO or NOx to NH₃, as shown in Figure 6.12. When NO and NOx pulsing times were 30 seconds, the conversions of NO and NOx on the lightly and highly aged catalysts were similar. When NO and NOx pulsing times were 60 seconds, the conversions of NO or NOx 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 NH₃ on the
catalyst and NO or NOₓ was not in large quantity, NO or NOₓ could be reduced and decreased catalyst
activity was not detected. However, when NO or NOₓ 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 NH₃. In last section it was concluded that both
weakly and strongly adsorbed NH₃ can react with NOₓ. Although aging has little effect on the quantity of
strongly adsorbed NH₃, the loss of weakly adsorbed NH₃ 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
NH₃ adsorption on a Cu-ZSM-5 catalyst. The data here do not demonstrate that NH₃ storage is the
degradation effect, but do suggest that it plays a role, as would be expected.

Figure 6.12 Effect of aging and NH₃/NOₓ ratio on the fast and standard SCR reactions; conditions:
250°C; NH₃ inlet concentration: 419 ppm; NOₓ inlet concentration: 416 ppm; time gap between NH₃
pulsing adsorption and NO pulse: 10 seconds;
a1: 60 seconds NH₃ pulse adsorption followed by a 60 second NO pulse on lightly aged catalyst;
a2: 60 seconds NH₃ 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 NOx (1:1 NO:NO$_2$) pulse on lightly aged catalyst;
b2: 60 seconds NH$_3$ pulse adsorption followed by a 60 second NOx (1:1 NO: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 NOx (1:1 NO:NO$_2$) pulse on lightly aged catalyst;
d2: 60 seconds NH$_3$ pulse adsorption followed by 30 seconds NOx (1:1 NO: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 NOx were introduced into the system. NH$_3$ adsorption and SCR reactions were conducted at 250°C. NO/NOx consumptions per unit length of catalyst are shown in Figure 6.13(a) and the cumulative of NO/NOx 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/NOx consumption when the NO and NOx introduced were less than the quantity of adsorbed NH$_3$. The resemblance of NO and NOx 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; NOx 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 NOx (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 NO₂ 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 NO₂ 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 O₂ 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, NH₃ 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 NH₃ supply since part of the NH₃ is oxidized by O₂ and equimolar amounts of NH₃ 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 NH₃ reacting with NOx rather than O₂.

3. NO₂-SCR with equimolar NH₃ and NO₂ feed results in significant N₂O production, and N₂O formation tends to decrease with increasing temperature above 250°C. At temperatures between 300 to 400°C, besides the N₂O formation route, other reactions contribute to decreased N₂O formation, including the decomposition of NH₄NO₃ into HNO₃ then to NO₂ and O₂, and/or NO₂ decomposition into NO and O₂. At high temperatures, both the enhanced NO₂-SCR to N₂ and N₂O decomposition at the back part of the catalyst contribute to decreased N₂O formation as well.

4. Different reaction patterns were observed for unbalanced NO:NO₂ ratios (≠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 NO₂-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\textsubscript{3} conversions changed monotonically with temperature and catalyst length. NH\textsubscript{3} overconsumption became significant when the reaction temperature was higher than 300\textdegree C, which limited the conversion of NO due to the lack of NH\textsubscript{3}. Therefore, for standard SCR and fast SCR, NO\textsubscript{x} conversion attained its maximum at 300\textdegree C. In fast and standard SCR, hydrothermal aging decreased reaction rates for SCR and NH\textsubscript{3} overconsumption simultaneously. Selectivity to NH\textsubscript{3} overconsumption was higher over the highly aged catalyst at high temperatures, >500\textdegree 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\textsubscript{3} concentrations. NO conversion under standard SCR conditions was more heavily affected by hydrothermal aging than NO\textsubscript{x} conversion for fast SCR. Correspondingly, NH\textsubscript{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\textsubscript{2} at the front of the catalyst. Hydrothermal aging decreased the extent of NO\textsubscript{2} decomposition into NO at high temperatures, which helped maintain fast SCR reaction conditions in the catalyst. The effect of hydrothermal aging on NH\textsubscript{3} oxidation was more complicated. Generally, aging reduced NH\textsubscript{3} oxidation activity, but it did not change monotonically with aging extent; neither did the output of NO\textsubscript{x} produced during NH\textsubscript{3} oxidation. However, the highly aged catalyst produced a higher proportion of NO\textsubscript{x}. At 200\textdegree C, hydrothermal aging did not show appreciable effects on the SCR extent with various NO:NO\textsubscript{2} ratios.

8. NH\textsubscript{3} adsorption profiles along a Cu-zeolite SCR catalyst, standard and fast SCR reactions over a NH\textsubscript{3}-precovered SCR catalyst and NH\textsubscript{3} migration were investigated. When NH\textsubscript{3} pulse times were short, and the front part of the catalyst far from saturation, NH\textsubscript{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\textsubscript{3} inlet concentration had a significant effect on the NH\textsubscript{3} adsorption profile. For the same amount of input NH\textsubscript{3}, a high NH\textsubscript{3} inlet concentration with a shorter pulse time resulted in a steeper NH\textsubscript{3} adsorption profile. Catalyst aging and increasing adsorption temperature reduced the amount of NH\textsubscript{3} stored, resulting in flatter NH\textsubscript{3} adsorption profiles for the same NH\textsubscript{3} input level.

9. The NH\textsubscript{3} profiles changed after the pulse ended, demonstrating NH\textsubscript{3} migration. There were at least two kinds of adsorbed NH\textsubscript{3}: weakly adsorbed NH\textsubscript{3} and strongly adsorbed NH\textsubscript{3}, both of which react with NO or NO\textsubscript{x}. Weakly adsorbed NH\textsubscript{3} desorbed and migrated within seconds,
while strongly adsorbed NH\textsubscript{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\textsubscript{3}, but did decrease the catalyst’s ability to adsorb weakly bound NH\textsubscript{3}. Also, catalyst aging increased the migration phenomenon of weakly adsorbed NH\textsubscript{3}. The effect of temperature on NH\textsubscript{3} migration was similar to that of catalyst aging.

10. NH\textsubscript{3} adsorption profiles were compared with NOx consumption profiles during the fast SCR reaction, run after the catalyst was exposed to NH\textsubscript{3}. NOx consumption profiles were flatter than their corresponding NH\textsubscript{3} adsorption profiles due to NH\textsubscript{3} migration. The NO and NOx consumption profiles during standard and fast SCR reactions on the catalyst pre-covered with NH\textsubscript{3} and having a similar NH\textsubscript{3} distribution were not different. Also, the effect of catalyst aging on the standard and fast SCR reactions after NH\textsubscript{3} exposure depended on the ratio of input quantities of NH\textsubscript{3} and NO or NOx. With higher NH\textsubscript{3} coverage, the effect of aging was insignificant. When the NO and/or NOx were greater than the available adsorbed NH\textsubscript{3}, the NO and/or NOx 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\textsubscript{3} depended on the ratio of input quantities of NH\textsubscript{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\textsubscript{3} adsorption and SCR reactivity models. Regarding NH\textsubscript{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\textsubscript{3} adsorption. It is quite possible that other established isotherms may not be able to describe the NH\textsubscript{3} adsorption and desorption process very well, because NH\textsubscript{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 NOx and differently adsorbed NH\textsubscript{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 NH₃ adsorption and temperature programmed desorption (TPD), NH₃ 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 NH₃ 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 NH₃ oxidation, standard SCR, and transient experiments with changing NO and NH₃ concentrations and NO₂ 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 NH₃ 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 Siliconert, 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 NH₃ consumed. When the downstream tubing temperature was 142°C, via providing extra heating, some conversion was noted but only with low H₂O levels.

AI.2.2 NH₃ adsorption and temperature programmed desorption
A key step in the reaction sequence is NH₃ adsorption on the catalyst. Therefore, the catalyst’s NH₃ storage capacity is critical to overall performance. In this experiment, the catalyst’s NH₃ adsorption capacity was measured and NH₃ desorption profiles as a function of temperature evaluated.

The space velocity was 15,000 hr⁻¹ (STP) and the inlet concentration of NH₃ was around 310 ppm. First, the catalyst was cleaned with 8% O₂, 5% H₂O, 5% CO₂ and a balance of N₂ at 500°C for 15 minutes. After cooling the reactor to 155°C, NH₃ was introduced into the system with 5% H₂O, 5% CO₂ and a balance of N₂. When the outlet NH₃ 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±3.9 μmol NH$_3$ per gram of catalyst adsorbed. During the temperature programmed desorption (TPD), 86.3±11.6 μmol 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±5.5 μmol/gram and 111±14.9 μmol/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)](image-url)
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 hr$^{-1}$. The concentrations of NH$_3$, O$_2$ and H$_2$O 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$_2$O concentration was also evaluated, with results also shown in Figure AI.3 for Fe-zeolite. Increasing H$_2$O 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 \(\text{NH}_3\) concentration, water content and oxygen concentration. Again, higher levels of \(\text{NH}_3\) led to less oxidation, but the extent of oxidation was higher over the Cu catalyst, reaching 100% conversions by 500°C.

Figure AL.2(a) Effect of \(\text{NH}_3\) concentration on \(\text{NH}_3\) oxidation (Fe-zeolite)
Figure AI.2(b) Effect of NH$_3$ concentration on NH$_3$ oxidation (Cu-zeolite)
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 A1.4 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 A1.6 Effect of NO concentration and temperature on NO to NO₂ conversion (Cu-zeolite)

A1.2.5 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 NOx 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 350ºC, which is in line with previous studies [106].

The effects of inlet O₂ and water concentrations on NO conversion are shown in Figure A1.9. The conversion of NO increases as the concentration of O₂ increases when the temperature was less than 300ºC, 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 500ºC, due to SCR and NH₃ oxidation. This leads to lower NO conversions at intermediate temperatures, although complete conversions were obtained at 500ºC, 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<sub>3</sub> concentration on NO conversion
(Fe-zeolite, NO concentration fixed at 450 ppm)

Figure AI.7(b) Effect of temperature and NH<sub>3</sub> 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 O\textsubscript{2} and H\textsubscript{2}O content on NO conversion
(Fe-zeolite, NH\textsubscript{3} = 473 ppm; NO = 450ppm)

**AI.2.6 SCR with NO and NO\textsubscript{2}**

The objectives of these experiments were to evaluate the effect of NH\textsubscript{3} concentration on the conversion of NH\textsubscript{3} and NO\textsubscript{x}, and investigate the effect of NO:NO\textsubscript{2} ratio on the conversion of NO\textsubscript{x} and the production of N\textsubscript{2}O. The ratio of NO:NO\textsubscript{2}, and inlet NH\textsubscript{3}, O\textsubscript{2}, 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\textsuperscript{-1}. The effect of the inlet NH\textsubscript{3} concentration and temperature on the conversion of NO\textsubscript{x} in the NO: NO\textsubscript{2} system was similar to that for the standard SCR reactions. The effect of NO:NO\textsubscript{2} ratio on NO\textsubscript{x} conversion is shown in Figure AI.10. When the ratio of NO:NO\textsubscript{2} is around 0.7 to 1.0, the conversion of NO\textsubscript{x} reached the maximum. As the NO:NO\textsubscript{2} ratio increased beyond that, the NO\textsubscript{x} conversion decreased, especially at low temperature.

When the ratio of NO:NO\textsubscript{2} was close to 1, the fast SCR reaction is likely dominant, thus the NO\textsubscript{x} conversion reached its maximum. When the ratio of NO:NO\textsubscript{2} is less or larger than 1, some fast SCR occurs, but so do the standard reaction and the reaction between NO\textsubscript{2} and NH\textsubscript{3}, which are relatively slower. At low temperature, the standard reaction is more kinetically limited than the fast reaction, and therefore, changing the NO:NO\textsubscript{2} is more significant. At higher temperatures, both reactions are kinetically fast and the effect of NO:NO\textsubscript{2} ratio on SCR reaction is not so outstanding.
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.

NH$_3$ 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 NH$_3$ was adsorbed per gram of catalyst. The peak in NH$_3$ desorption occurred at 306°C. For Cu-zeolite, 117±11 μmol of NH$_3$ was adsorbed per gram of catalyst. The peak in NH$_3$ desorption occurred at 225°C. The higher peak desorption temperature for Fe-zeolite indicated that the bonding between NH$_3$ and Fe-zeolite is stronger than that between NH$_3$ and Cu-zeolite.

The effects of NH$_3$, H$_2$O, and O$_2$ inlet concentrations on NH$_3$ 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 NH$_3$ concentration led to less oxidation, indicating that NH$_3$ might be inhibiting NH$_3$ oxidation on Fe-zeolite. However, increasing O$_2$ concentration led to increased NH$_3$ 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, H$_2$O, and O$_2$ 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 $O_2$ content, and decreased with increasing water content. Similar trends were found for Cu-zeolite regarding the effect of NO, $H_2O$ and $O_2$ inlet concentrations.

In the standard SCR reaction, NO conversion is a function of inlet $NH_3$ and NO concentration, as well as temperature. Over the Fe-zeolite catalyst, $NH_3$ and NO concentration effects are related to NO:$NH_3$ ratios. NO conversion increased with temperature. When the $NH_3$ concentration was higher than that of NO, the NO conversion reached 100% at around 350°C. The conversion of NO increased with $O_2$ inlet content when the temperature was lower than 300°C. Similar trends were observed over the Cu-zeolite catalyst. However, the oxidation of $NH_3$ was more extensive over the Cu catalyst. A significant amount of $N_2O$ was also produced as the NO:$NH_3$ conversion increased.

The effect of NO:NO$_2$ ratio on NOx conversion was examined. When the ratio of NO:NO$_2$ was around 0.7 to 1.0, the NOx conversion reached the maximum. At low temperature, the standard reaction is more kinetically limited than the fast reaction. Therefore, changing the NO:NO$_2$ was more significant. At higher temperatures, both reactions are kinetically fast and the NO:NO$_2$ 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 through 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](image)

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.
The governing equations are as follows.

For the conservation of momentum,

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

Where $\mathbf{F} = 0$ since gravity was not considered. As the main contents of the gas were $\text{N}_2$, $\text{O}_2$ and $\text{CO}_2$, the gas properties, such as density and viscosity, can be represented by those of air.

For the conservation of mass,

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

where

- $\rho$ is the density of air at 523K,
- $\mu$ 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, and the pressure at the outlet is \( 1.2532 \times 10^5 \) Pa.
The pressure at the front of the catalyst channel was calculated to be \( 1.2533 \times 10^5 \) 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,
\[
D = C \times 60 \times 4
\]
Considering the effect of temperature on volume flow rate, values in Column E can be calculated as,
\[
E = D \times \frac{273}{523}
\]
The total volume flow rate through the channel is 44ml/min at 273K, so we have
\[
F = 44 - E
\]
\[
G = F \times \left( \frac{523}{273} \right)
\]
\[
H = \frac{G \times 10^6}{(60 \times (0.2550 \times 10^6))}, \text{ where } 0.2550 \times 10^6 \text{ is the area of the capillary cross section.} 
\]
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.

\[ J = 100\% \times \frac{(I-C)}{C} \]

**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

| 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 273K (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,

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

(AIII.1)

Where \( F = 0 \), 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,

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0
\]

(AIII.2)

where 
\( \rho \) is the density of air at 523K,
\( \mu \) 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 \( u = 0.4911 \text{ m/s} \) at 523K, and the pressure at the outlet is \( 1.2532 \times 10^5 \text{ Pa} \).

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,

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{u}) = \nabla \cdot (D_{F,i} \nabla c_i) + R_i + S_i
\]  

Here \( c_i \) is the concentration of species \( i \), mol/m\(^3\);
\( D_{F,i} \) is the fluid phase diffusion coefficient, m\(^2\)/s;
\( R_i \) denotes a reaction rate expression, mol/m\(^3\)·s; and
\( S_i \) is an arbitrary source term for species \( i \), mol/(m\(^3\)·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:

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

Where \( \varepsilon \) is the porosity;
\( \rho_b \) is the bulk density, \( \rho_b = (1-\varepsilon)\rho_p \);
\( \rho_p \) is the solid phase density, kg/m\(^3\);
\( c_{p,i} \) is the species mass absorbed to solids, mol/kg(solid);
\( D_{D,i} \) is the coefficient for dispersion, m\(^2\)/s;
\( D_{e,i} \) is the effective diffusion coefficient considering the effect of tortuosity and porosity, m\(^2\)/s.

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

\[
-n \cdot D_{s,i} \nabla c_{i,u} = \frac{D_{s,i}}{d_s} (c_{i,u} - c_{i,d})
\]  

\[
-n \cdot D_{s,i} \nabla c_{i,d} = \frac{D_{s,i}}{d_s} (c_{i,d} - c_{i,u})
\]  

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 NH\(_3\) 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 NH\(_3\) pulsing adsorption only experiments, the net result
of the adsorption and desorption processes is the reduction of \( \text{NH}_3 \) 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, \( c_i \).

\[
c_{p,j} = \frac{k_L c_{p,max,j} c_i}{1 + k_L c_i},
\]

(AIII.7)

\[
\frac{\partial c_{F,j}}{\partial c_i} = \frac{k_L c_{p,max,j}}{(1 + k_L c_i)^2}
\]

(AIII.8)

Where \( C_{p,max} \) is the adsorption maximum, mol species per mass solid, and \( K_L \) is the Langmuir constant, \( \text{m}^3/\text{mol} \). 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,

\[
D_{e,j} = \varepsilon \tau_{F,j} D_{F,j}
\]

(AIII.9)

Where \( D_{F,i} \) is the single phase diffusion coefficient for the species in the fluid phase, \( \text{m}^2/\text{s} \); \( \tau_{F,j} \) is the tortuosity factor, unitless; \( \varepsilon \) is the porosity.

An initial condition is the \( \text{NH}_3 \) initial concentration is 0 mol/m\(^3\).

Boundary conditions for the Species Transport in Porous Media are,

Inlet concentration 0.009763 mol/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 \( \text{NH}_3 \) concentration along the length of monolith channel is shown in Figure AIII-2, where \( \text{NH}_3 \) concentration distribution snapshots at the pulsing time of 30s, 60s, and 90s
are shown. The picture indicates the progress of NH₃ concentration in the gas phase as pulsing time increased. At the beginning of NH₃ pulsing adsorption, there was no NH₃ on the catalyst surface. The driving force for NH₃ adsorption was high and thus more NH₃ was adsorbed. As the pulse time increased, NH₃ accumulated on the catalyst surface at the front end and the driving force for NH₃ adsorption in the front decreased and more NH₃ moved to the downstream of the flow.

The quantity of adsorbed NH₃ on the catalyst surface was calculated based on the change of NH₃ concentration in the gas phase. The comparison between the experimental data and modeling NH₃ storage on the catalyst is shown in Figure AIII-3. The trends in both sets of data are pretty similar. For the storage of NH₃ 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 NH₃ concentration became smaller at the end of the channel, and only a small portion of the flow was sampled, the detected NH₃ concentration in the gas phase for the latter part of the channel was probably approximately zero earlier than what actually was. Therefore, no NH₃ 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 NH₃ 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 NH₃ concentration distribution along the channel length

Figure AIII.3 Comparison between experimental and modeling NH₃ storage on the catalyst
Appendix IV Error Estimation

AIV.1 NH$_3$ TPD test

To check the repeatability of the test results for the adsorption and desorption of NH$_3$ on the zeolite based catalyst, repeat tests were done. The data are shown in Table AIV-1(a) and (b).

Table AIV-1(a) NH$_3$ adsorption and desorption on Fe-zeolite, sample 1

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$ Stored (10$^{-3}$mol)</th>
<th>NH$_3$ Desorbed (10$^{-3}$mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>2.127</td>
<td>2.071</td>
</tr>
<tr>
<td>Test 2</td>
<td>2.142</td>
<td>2.208</td>
</tr>
<tr>
<td>Average</td>
<td>2.135</td>
<td>2.139</td>
</tr>
<tr>
<td>σ</td>
<td>0.011</td>
<td>0.097</td>
</tr>
</tbody>
</table>

Table AIV-1(b) NH$_3$ adsorption and desorption on Fe-zeolite, sample 2

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$ Stored (10$^{-3}$mol)</th>
<th>NH$_3$ Desorbed (10$^{-3}$mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>2.888</td>
<td>2.469</td>
</tr>
<tr>
<td>Test 2</td>
<td>2.782</td>
<td>2.318</td>
</tr>
<tr>
<td>Average</td>
<td>2.835</td>
<td>2.394</td>
</tr>
<tr>
<td>σ</td>
<td>0.075</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Both cases indicate that the test error for NH$_3$ adsorption is smaller than that for desorption. This is due to the fact that adsorption time is short and the detected concentration of NH$_3$ is relative high. For the process of desorption, the time is long and the detected concentration of NH$_3$ is low for the later part of the test.

AIV.2 Spatial resolution

For spatial resolution, the initial concentration of NO, NO$_2$, and NH$_3$ 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, NO$_2$ and NH$_3$ concentration was 2.21, 4.20, and 2.23 ppm respectively.
Table AIV-2 Error estimate for NO, NO$_2$ and NH$_3$ concentration in spatial resolution tests

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>NO (ppm)</th>
<th>NO$_2$ (ppm)</th>
<th>NH$_3$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>179</td>
<td>201.5459</td>
<td>199.0101</td>
<td>392.4108</td>
</tr>
<tr>
<td>182</td>
<td>201.139</td>
<td>207.0291</td>
<td>397.0883</td>
</tr>
<tr>
<td>182</td>
<td>198.2711</td>
<td>199.0419</td>
<td>395.9665</td>
</tr>
<tr>
<td>192</td>
<td>198.9434</td>
<td>203.3502</td>
<td>393.3978</td>
</tr>
<tr>
<td>193</td>
<td>199.7898</td>
<td>197.224</td>
<td>392.3151</td>
</tr>
<tr>
<td>242</td>
<td>202.6119</td>
<td>204.4666</td>
<td>392.1116</td>
</tr>
<tr>
<td>245</td>
<td>201.3934</td>
<td>204.875</td>
<td>391.4678</td>
</tr>
<tr>
<td>246</td>
<td>195.3953</td>
<td>191.3985</td>
<td>388.7484</td>
</tr>
<tr>
<td>297</td>
<td>203.1552</td>
<td>203.4023</td>
<td>390.7637</td>
</tr>
<tr>
<td>298</td>
<td>200.606</td>
<td>201.39</td>
<td>390.1049</td>
</tr>
<tr>
<td>298</td>
<td>204.0135</td>
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</tr>
<tr>
<td>407</td>
<td>203.4188</td>
<td>201.0086</td>
<td>392.9679</td>
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<tr>
<td>516</td>
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<tr>
<td>516</td>
<td>202.9418</td>
<td>205.6196</td>
<td>392.2859</td>
</tr>
<tr>
<td>Average</td>
<td>201.1117</td>
<td>202.3453</td>
<td>392.4094</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>2.214601</td>
<td>4.195845</td>
<td>2.225991</td>
</tr>
</tbody>
</table>

AIV.3 NH$_3$ pulsing adsorption and SCR reactions

Table AIV-3 shows an example of the error estimate in the data obtained during the NH$_3$ pulsing adsorption and SCR reaction tests, where NH$_3$ was introduced into the system in a pulse mode for 60 seconds and NOx was introduced into the system for 30 seconds. The consumption of NOx was detected.
Table AIV-3 Example of the error estimate for NH$_3$ pulsing adsorption and SCR reactions

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

The data show that the test errors for NH$_3$ 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 NH$_3$ storage or NOx conversion.
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