Durable Zeolite Based Catalyst Systems for Diesel Emission Control

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Durable Zeolite Based Catalyst Systems for Diesel Emission Control

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Preface

Submission of this thesis is part of the candidature for the Ph.D. degree from the Technical University of Denmark (DTU). The contents of the thesis is the outcome of the work that has been carried out for the past three years, since the project started on May 15th 2015. The project was initially a collaboration between the CHEC (Combustion and Harmful Emission Control) centre of the Department of Chemical and Biochemical Engineering at DTU, and the Automotive department of Haldor Topsøe A/S with Prof. Anker D. Jensen and Dr. Ton V. W. Janssens as supervisors, respectively. Since the acquisition of the Automotive department by the Umicore organization, the industrial partner of the project has been Umicore Denmark ApS, at which the final year of the project has been carried out without changes to the supervisor team. The Innovation Fund Denmark (grant number 5139-0023B) is gratefully acknowledged for financial support throughout the duration of the project.

First, I would like to state my gratitude to my supervisors Prof. Anker D. Jensen and Dr. Ton V. W. Janssens for their guidance, support, dedication and interest, which has made it a pleasure to be a PhD student. I highly appreciate the professionalism and meticulousness that Anker represents, and his ever good spirits. A particular thank you to Ton, for enthusiastically sharing his wide technical knowledge within chemical engineering, chemistry, physics, for teaching me “pirate experiments” (I will miss those!), and for our discussions on results and many other technical and non-technical things – I am deeply grateful. Another person, without whom this project would not have materialized, is Dr. Peter N. R. Vennestrøm, who has acted as an unofficial co-supervisor. I am profoundly thankful for his priceless contributions to the project, and his continuous care, guidance and challenging questions. Also, I would like to thank Dr. Pär L. T. Gabrielsson for supporting the project and providing a place for it in his department, and for help establishing a good professional network.

The predominant part of the project was spent in Haldor Topsøe A/S, where I have been fortunate to be surrounded by many intellectual, helpful and kind people. I would like to thank Renato, Juan, Andrea, Dani, Malthe, Logi and Pablo from the “PhD office” for the enjoyable conversations in this international and diverse crowd, who gladly shared their experiences as PhD students, and made the coffee breaks and lunches very cheerful. I will also take the opportunity to thank Gitte Marquardt for introducing me to the “TPX4”, and for the relaxed chats while she aided the clean-up of most of the reactor setup after my sulfurous experiments clogged the system again (and again...). A great thanks to Dr. Pablo Beato for collaboration and insightful discussions about the NH$_3$-SCR mechanism, to Dr. Hanne Falsig for DFT calculations, to Dr. Søren B. Rasmussen for help with spectroscopic experiments, to Dr. Ramchandra Tiruvalarm for microscopy work, to Brian Jensen for showing me zeolite synthesis, and to the Analysis Lab for numerous S and Cu analyses.

At Umicore Denmark ApS I gratefully acknowledge Jesper S. Larsen for his invaluable help with conducting an extensive amount of SO$_2$-exposures, and for ensuring some great guitar solos in the test lab.
Furthermore, I have had the pleasure to take part in collaborations with other spectroscopic research groups, which has been most illuminating. For that, I want to thank Dr. Chiara Negri, Assoc. Prof. Gloria Berlier and Prof. Silvia Bordiga from the University of Turin, and Dr. Anita L. Lundager and Assoc. Prof. Susanne Mossin from DTU Chemistry. After an intense experimental stay at the University of Houston, my warmest (like Houston in July) appreciations go to Dr. Yasser Jangjou for the great and efficient collaboration in the lab and interesting football discussions, and to Prof. William S. Epling for his valuable scientific input and for introducing me to Corn Hole at the 8th Wonder.

Finally, I would like to express my deepest gratitude to all of my family for always supporting me in my studies and taking (or faking?) interest in my work. The most loving and profound thanks to my wonderful wife Pernille for her unconditional love and support, which was ever present while also giving birth to our two dear daughters, who taught me efficiency and the value of a good night’s sleep.
Abstract

Diesel vehicles are widely used for transportation of people and goods, which is responsible for a significant consumption of diesel, and the associated release of mainly CO$_2$, but also pollutants such as CO, hydrocarbons, soot particles and NO$_x$ (x = 1,2). These pollutants threat the health of humans and negatively affect the environment, and therefore, abatement is enforced by legislation, which is practically handled by installation of exhaust aftertreatment systems in passenger cars as well as in heavy-duty vehicles. A crucial component of the aftertreatment systems is the catalyst for selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR). Current state-of-the-art SCR catalysts are zeolite-based Cu-CHA materials, which is mainly due to their unmatched low-temperature activity. Unfortunately, the presence of 0.5-2 ppmv of SO$_2$ in diesel exhaust significantly inhibits the low-temperature activity Cu-CHA catalysts, which diminishes the NO$_x$ removal efficiency. In order to comply with current and future NO$_x$ emission limits, development of more SO$_2$ resistant Cu-CHA catalyst systems is necessary, which requires a better fundamental understanding of the deactivation of Cu-CHA catalysts by SO$_2$.

In this work, Cu-CHA catalysts have been produced and exposed to SO$_2$ in various gas mixtures at different temperatures (200-550 °C), and exposure times, to investigate the effects of SO$_2$ at the various conditions of an aftertreatment system. The uptake of S, determined from elemental analysis and adsorption/desorption measurements, has been compared to the impact on the catalytic performance in the NH$_3$-SCR reaction after the different SO$_2$ exposures, and after regeneration at 550 °C in SO$_2$-free gas. In parallel, characterization with scanning transmission electron microscopy – energy dispersive X-ray (STEM-EDX) spectroscopy and electron paramagnetic resonance (EPR) spectroscopy have been used to assess the location of S, and density functional theory (DFT) calculations have been carried out to determine possible Cu,S species.

The deactivation is established to be the result of formation of Cu,S species, and not a consequence of ammonium sulfate precipitation, since the S/Cu ratio has not been observed to significantly exceed 1. Some Cu,S species decompose below 550 °C (reversible), while a more stable Cu sulfate species (irreversible) that decomposes around 650 °C, can form on a restricted fraction of the Cu. Formation of the different Cu,S species is dependent on several conditions such as the oxidation state of Cu, the temperature, and the presence of H$_2$O and SO$_3$. DFT calculations suggested that SO$_2$ adsorbs more stably on Cu$^+$, while SO$_3$ preferably reacts with Cu$^{II}$, which was consistent with experimental data. At 200 °C it was observed that the formation of Cu,S species is enhanced by co-feeding SO$_3$, whereas at 550 °C there is no measurable impact. In the same experiments, the presence of H$_2$O enhanced the formation of irreversible Cu sulfate at both 200 and 550 °C, but had no impact on the formation of reversible Cu,S species.

While there is no apparent impact of the chemical composition of the CHA framework (H$_n$Al$_n$Si$_{3-n}$O$_2$ vs H$_n$Si$_n$AlP$_{1-n}$O$_4$), the Cu$^{II}$ sites associated with one or two framework Al centers, Z-CuOH and Z$^*_2$-Cu, respectively, have different resistance towards SO$_2$, as indicated by DFT calculations. The EPR characterization indirectly showed that mainly Z-CuOH reacts with SO$_3$ to formation of the reversible Cu,S species, whereas certain Z$_2$-Cu sites were directly seen to participate in the
formation of irreversible Cu sulfate. Finally, other Z\textsubscript{2}-Cu sites were inert to SO\textsubscript{2} exposure, which explains why a 100% deactivation has not been observed.

In terms of the impact of reversible and irreversible Cu,S species on the NH\textsubscript{3}-SCR activity, the deactivation inferred by the reversible Cu,S species was always disproportionately larger than the S/Cu ratio, and caused a lowering of the apparent SCR activation energy with increasing S/Cu ratio. In contrast, the remaining irreversible Cu,S species after regeneration exhibited a 1:1 correlation between the deactivation and S/Cu ratio, as well as the apparent activation energies were restored to the same level as the fresh catalyst. The deactivation occurs by exposure to 1.5 ppmv SO\textsubscript{2}, and by increasing the SO\textsubscript{2} concentration and simultaneously decreasing the exposure time correspondingly, similar deactivation levels are reached. Hence, it appears to depend on the product of the SO\textsubscript{2} concentration and exposure time. Accelerated SO\textsubscript{2} exposures showed that the deactivation occurs fast, reaching at least 80% before 5% of the lifetime SO\textsubscript{2} exposure. However, the deactivation could at all times be lowered to about 20%, which is probably dependent on the specific Cu-CHA catalyst. Thus, the application of Cu-CHA catalysts in aftertreatment systems is contingent on regeneration.

A new method to quantify the active amount of Cu in Cu-CHA catalysts by measuring the NO consumption during a temperature-programmed reduction in NO+NH\textsubscript{3} has been developed (NO-TPR). The method is applicable on regenerated catalysts, and potentially also on SO\textsubscript{2} exposed catalysts.
Person- og godstransport har ført til stor anvendelse af dieseldrevne biler og lastbiler, som er ansvarlige for en anseeligt forbrug af diesel, og den medfølgende udledning af CO₂, CO, kulbrinter, sodpartikler og NOₓ \((x = 1,2)\), som forurener miljøet og er skadelige for menneskers helbred. For at mindske udledningen, er der indført lovgivning som definerer maksimum grænser for udledningen af disse stoffer, hvilket har medført udvikling og implementering af udstødningssystemer. For at imødekomme de nuværende, og fremtidige, emissionsgrænser for NOₓ, er det nødvendigt effektivt at kunne anvende selektiv katalytisk reduktion med NH₃ (NH₃-SCR), hvilket bedst opnås over zeolit-baserede Cu-CHA katalysatorer, grundet deres særligt høje aktivitet i lav-temperaturintervalliet for NH₃-SCR. Tilstødningsgassen af selv 0.5-2 ppmv SO₂ i udstødningsgassen har en negativ indvirkning på Cu-CHA katalysatorers lav-temperatur aktivitet, hvilket betydeligt forringer NOₓ fjernelsen. For at kunne leve op til nuværende og fremtidige NOₓ emissionsgrænser, er det nødvendigt at udvikle mere SO₂ robuste Cu-CHA katalysatorer, hvilket kræver en bedre grundlæggende forståelse af hvordan SO₂ forårsager deaktivering af disse katalysatorer.

Det eksperimentelle arbejde udført i dette projekt har inkluderet fremstilling af pulver Cu-CHA katalysatorer, som er blevet eksponeret til SO₂ i forskellige gassammensætninger ved varierende temperaturer (200-550 °C) og eksponeringstider. Indflydelsen af svovl er blevet undersøgt ved at måle svovlindholdet med elementaranalyse og adsorption/desorption, og sammenholde dette med ændringerne i den katalytiske aktivitet efter de forskellige SO₂ eksponeringer, og efter regenerering ved 550 °C uden SO₂ i gassen. Sidenløbende er prøverne blevet karakteriseret med forskellige spektroskopiske metoder såsom STEM-EDX (scanning transmission electron microscopy – energy dispersive X-ray) og EPR (electron paramagnetic resonance) for at bestemme hvor i Cu-CHA katakysatorerne at svovl befinner sig, og DFT (density functional theory) beregninger blevet udført for at identificere mulige Cu₃S forbindelser.

Årsagen til at Cu-CHA katalysatorer deaktiverer i tilstødningsprocessen af SO₂, skyldes dannelse af Cu₃S forbindelser, og ikke udfældning af poreblokerede ammoniumsulfat, hvilket bekræftes ved at der endnu ikke er målt S/Cu forhold, som er signifikant højere end 1. Nogle af disse Cu₃S forbindelser dekomponerer ved lavere temperaturer end 550 °C (reversibile), men også en mere stabil Cu sulfat (irreversibel) forbindelse dannes på en mindre fraktion af Cu, som dekomponerer ved ca. 650 °C. Dannelsen af både reversible og irreversible Cu₃S forbindelser afhænger af betingelserne, hvorfra de dannes, og både Cu oxidationstrinnet, temperaturen, og tilstødningsprocessen af SO₃ og H₂O en indflydelse på dette. Konsistent med eksperimentelle resultater, viser DFT beregninger at SO₂ har en større affinitet for CuI end CuII, hvilket er omvendt for SO₃. Temperaturen har en indirekte indflydelse på dette, idet CuII reduceres til CuI af NO og NH₃, som primært findes ved lavere temperaturer hvor SCR reaktionshastigheden er lavere. Ved lav temperatur (200 °C) fører SO₂-holdig gas til en markant hurtigere dannelse af Cu₃S forbindelser, imens det ved 550 °C ikke har nogen målbar indflydelse grundet den højere oxidationshastighed af SO₂ ved højere temperaturer. Af samme eksperimenter med eksponering ved 200 og 550 °C, fremgik det at tilstødningsprocessen af H₂O fremmer dannelsen af irreversibel Cu sulfat, men ingen betydning har for dannelsen af reversible Cu₃S forbindelser.
DFT viste at indflydelsen af forskellige kemiske sammensætninger af CHA strukturen (H₆Al₆Si₁₄O₄ vs H₆Si₆AlP₁₄O₄₄) er minimal, men at Cu⁺⁺ placeret i nærheden af ét (Z-CuOH) eller to (Z₂-Cu) Al centre i zeolitstrukturen, fører til store forskelligheder i affiniteten for SO₂ og SO₃. Dette blev bekræftet med EPR, som indirekte viste at primært Z-CuOH reagerer med SO₂ og laver reversible Cu,S forbindelser, hvorimod det direkte kunne ses at kun nogle Z₂-Cu kunne reagere med SO₃, og lave irreversible Cu sulfat. Den resterende del af Z₂-Cu forbrygtes upåvirket af SO₂ eksponeringen, hvilket kunne forklare hvorfor en 100% deaktivering endnu ikke er observeret.

Effekten af de reversible og irreversible Cu,S forbindelser på NH₃-SCR aktiviteten var vidt forskellig. Således medførte de reversible Cu,S forbindelser altid en disproportional højere deaktivering end S/Cu forholdet, samt at aktiveringseffekten faldt med øgede S/Cu forhold. modsat var der umiddelbart en 1:1 afhængighed mellem den irreversible deaktivering og S/Cu forhold, og efter regenerering var aktiveringseffekten tilbage på niveau med aktiveringseffekten for den friske katalysator.Det blev observeret at deaktivering steg ved eksponering til 1.5 ppmv SO₂, og at samme deaktivering kunne opnås ved at høje SO₂ koncentrationen ved samtidigt at forkorte eksponeringstiden tilsvarende. Derfor afhænger deaktiveringstiden tilsyneladende af produktet af SO₂ koncentrationen og eksponeringstiden. Accelererede SO₂ eksponeringer viste at allerede før man når 5%, af det der svarer til en livstidseksponering for en katalysator i et udstødningssystem, er deaktivering over 80%. Dog kunne deaktiveringstiden altid mindskes til ca. 20% ved regenerering, hvilket betyder at lav-temperaturaktiviteten af Cu-CHA katalysatorer kan uddybes i udstødningssystemer, såfremt de bliver effektivt regenereret.

En ny metode til at kvantificere mængden af aktivt Cu i Cu-CHA katalysatorer er blevet introduceret, hvor forbruget af NO måles i løbet af en temperatur-programmeret reduktion (NO-TPR) i NO og NH₃. Med mindre ændringer virker denne metode også til at være anvendelig på SO₂ eksponerede og regenererede Cu-CHA katalysatorer.
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Chapter 1

Introduction
Motivation

During the past thirty years, there has been an increasing focus on the impact of energy consumption on the Earth’s climate and the public health. The realizations that burning fossil fuels leads to global warming through accumulation of CO$_2$ in the atmosphere, and has a negative impact on air quality, have become focus points of environmental concerns around the world. An important part of the energy consumption lies in the transportation sector, which was responsible for 23% of the global anthropogenic CO$_2$ emissions in 2010 [1], and therefore a major contributor to the environmental challenges we are facing today.

Among the different sectors of transportation, i.e. aviation, marine, railway, and road, the road vehicles generate 74% of the CO$_2$ emissions [1]. Gasoline and diesel are the major fuels used for light-duty and heavy-duty vehicles, with CO$_2$ and H$_2$O as the major products of fuel combustion. Furthermore, exhaust gases also contain small amounts of byproducts, which are NO$_x$ (NO and NO$_2$), unburned hydrocarbons (HC), CO, soot particles, and SO$_2$. The typical concentrations of these are listed in Table 1. The production of CO, HC, and soot particles is a consequence of incomplete combustion, while SO$_2$ is formed from oxidation of sulfur bound in the fuel and engine lubricants. NO$_x$ is formed by oxidation of the nitrogen in the air at high temperatures during the combustion of fossil fuels, where air is used for supplying oxygen.

<table>
<thead>
<tr>
<th>CO$_2$ [vol%]</th>
<th>H$_2$O [vol%]</th>
<th>O$_2$ [vol%]</th>
<th>CO [ppmv]</th>
<th>HC [ppmv]</th>
<th>PM [mg/km]</th>
<th>NO$_x$ [ppmv]</th>
<th>SO$_2$ [ppmv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-12</td>
<td>2-12</td>
<td>3-17</td>
<td>10-500</td>
<td>20-300</td>
<td>10-100</td>
<td>50-1000</td>
<td>0.5-2</td>
</tr>
</tbody>
</table>

Even though the concentrations of CO, HC, soot, SO$_2$ and NO$_x$ in the exhaust from vehicles are low, their environmental impact is significant. To reduce the impact of our energy consumption on the environment, the emission of these components is regulated. In Europe, the current regulations are the EURO 6d-TEMP for light-duty vehicles and EURO VIId for heavy-duty vehicles, which are listed in Table 2 [3].
Table 2 – Emission standards for CO, hydrocarbons (HC), particulate matter (PM), particulate number (PN), NO\textsubscript{x} (NO+NO\textsubscript{2}), and SO\textsubscript{2} for light-duty (EURO 6d-TEMP) and heavy-duty vehicles (EURO VId), which are tested for steady-state and transient emissions in the world harmonized steady-state cycle (WHSC) and the world harmonized transient cycle (WHTC).

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>EURO 6d (Light-duty)</th>
<th>EURO VId (Heavy-duty diesel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO [g/km]</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>HC [g/km]</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>HC+NO\textsubscript{x} [g/km]</td>
<td>-</td>
<td>0.17</td>
</tr>
<tr>
<td>PM [g/km]</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>PN [#/km]</td>
<td>(6.0 \cdot 10^{11})</td>
<td>(6.0 \cdot 10^{11})</td>
</tr>
<tr>
<td>NO\textsubscript{x} [g/km]</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>SO\textsubscript{2} [wt ppm in diesel]</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

For gasoline cars, the emissions of CO, HC, and NO\textsubscript{x} are handled by a three-way catalyst, based on noble metals (Pd, Pt, Rh), sometimes assisted by a lean-NO\textsubscript{x} trap to further reduce the emission of NO\textsubscript{x}. Modern gasoline cars, with direct fuel injection, also produce soot [4–6], which has prompted the implementation of soot filters on gasoline cars, similar to diesel vehicles [3]. This regulation has been effective since 01.09.2018 in Europe.

The technology used for exhaust gas treatment in gasoline cars only works for combustion with fuel/air mixtures close to the stoichiometric concentrations. Diesel engines always operate under fuel-lean conditions with a larger excess of air, which means that the exhaust gas contains a substantial amount of oxygen (3-17% [2]), which prohibits the use of the three-way catalyst used in gasoline cars. Diesel engines are inherently more effective compared to gasoline engines, leading to lower emissions of CO\textsubscript{2} from diesel engines. They find application in passenger cars, mainly in Europe, trains, off-road machinery, and heavy-duty vehicles.

Worldwide, a significant source of NO\textsubscript{x} emissions is from heavy-duty diesel vehicles [1]. NO\textsubscript{x} is a major cause of air pollution, and emissions of NO\textsubscript{x} to the atmosphere contributes to the formation of smog, acid rain and ozone [7], which threaten the health of humans as well as the local and global environment [1,7]. Therefore, it is important to minimize the emissions of NO\textsubscript{x}, which is the motivation for this work. Aftertreatment systems are installed in heavy-duty vehicles in order to limit the emissions of the polluting compounds from the exhaust. The current technology for diesel exhaust gas treatment, to comply with the required emissions, is shown in Figure 1. The aftertreatment system consists of a diesel oxidation catalyst (DOC), a diesel particulate filter
(DPF), a catalyst for selective catalytic reduction of NO\textsubscript{x} with ammonia (NH\textsubscript{3}-SCR), and an ammonia slip catalyst (ASC). The DOC catalyzes the oxidation of CO and unburned hydrocarbons to CO\textsubscript{2} and NO to NO\textsubscript{2}, while the DPF captures particulate matter. As the carbonaceous particulate matter accumulates on the DPF, regeneration of the DPF is necessary. This is done by burning off the particles in active or passive regeneration. In active regeneration, the temperature of the system is increased to well over 500-700 °C. This is achieved via the release of heat from the exothermic oxidation of additional diesel injected to the DOC. Passive regeneration exploits that the NO\textsubscript{2} formed in the DOC can burn off the soot particles in the temperature range 350-500 °C, which is in the normal operating window for a DPF. In both active and passive regeneration, the function of the DOC is important for an effective operation of the DPF.

The most efficient removal of NO\textsubscript{x} from exhaust gas is achieved with the NH\textsubscript{3}-SCR reaction. In this reaction, NH\textsubscript{3} selectively reduces NO to N\textsubscript{2} and H\textsubscript{2}O in the presence of O\textsubscript{2}, according to Eq. (1). Diesel exhaust typically contains NO in the concentration range 50-1000 ppmv and O\textsubscript{2} in the range 3-17 vol%, as well as 2-12 vol% of H\textsubscript{2}O from the air [2].

\[
4\text{NO} + 4\text{NH}_3 + 2\text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \tag{1}
\]

In an exhaust aftertreatment system, the removal of NO\textsubscript{x} takes place over the NH\textsubscript{3}-SCR catalyst. The NH\textsubscript{3} is usually supplied by injection of an aqueous solution of urea upstream to the NH\textsubscript{3}-SCR catalyst, which thermally decomposes to NH\textsubscript{3} and CO\textsubscript{2} above 180 °C. In order to prevent emission of unreacted ammonia (ammonia slip) from the NH\textsubscript{3}-SCR reaction, any excess NH\textsubscript{3} is removed by the ASC downstream to the SCR catalyst.

The removal of NO\textsubscript{x} in the aftertreatment system takes place in the temperature range 180-550 °C. The lower limit of 180 °C is determined by the decomposition temperature of urea to generate the NH\textsubscript{3}. Catalysts for automotive NH\textsubscript{3}-SCR are based on V\textsubscript{2}O\textsubscript{5} and Fe- or Cu-containing zeolites. The overall performance of these catalysts is based on the catalytic activity and robustness in the harsh conditions of an aftertreatment system. The activity of the catalysts in the 180-550 °C
temperature window is of course of high importance as this determines the NO\textsubscript{x} removal efficiency. Fe-zeolites and V\textsubscript{2}O\textsubscript{5}-based SCR catalysts become active in the NH\textsubscript{3}-SCR reaction above 250 °C, as seen in Figure 2, while the Cu-zeolites are active already from 180 °C [9]. In order to comply with current and future NO\textsubscript{x} emission limits, efficient NO\textsubscript{x} removal in the entire temperature range is necessary. As the engine efficiency is continuously improved in order to lower the CO\textsubscript{2} emissions, consequently, the exhaust becomes colder. Thus, efficient NO\textsubscript{x} removal in the low-temperature region becomes increasingly important. For example, 63\% of the accumulated NO\textsubscript{x} emissions from a EURO VI heavy-duty vehicle during a 3 h mixed drive (48\% urban, 17\% rural, 35\% highway) occurred during the first 23 min where the aftertreatment system was still heating [10]. Therefore, the unmatched low-temperature activity of Cu-zeolites makes these catalysts the best candidates for achieving the most efficient NO\textsubscript{x} removal for automotive aftertreatment systems.

**Figure 2 – Steady-state NO conversion as function of temperature for catalysts samples of Cu-zeolites (Cu-CHA), Fe-zeolites (Fe-β), and V\textsubscript{2}O\textsubscript{5}-based automotive NH\textsubscript{3}-SCR catalysts, which serve to illustrate the differences between these catalyst materials as described in Chapter 8 in [9].**

Current state-of-the-art Cu-zeolite catalysts for NH\textsubscript{3}-SCR are based on the chabazite (CHA) framework (Cu-CHA) [9,11–14]. The CHA framework has a small-pore structure consisting of 4-, 6-, and 8-membered rings (see Figure 3). The best known materials with CHA structure are the SSZ-13 zeolite (H\textsubscript{n}Al\textsubscript{n}Si\textsubscript{1-n}O\textsubscript{2}) and the alumino-phosphate based SAPO-34 (H\textsubscript{n}Si\textsubscript{n}AlP\textsubscript{1-n}O\textsubscript{4}).
In the SSZ-13 zeolite, the microporous structure arises from a certain 3-dimensional combination of tetrahedral building units of Si$^{4+}$ coordinated to 4 oxygen atoms. If a Si$^{4+}$ is substituted with an Al$^{3+}$, a local negative charge is induced in the framework, as illustrated in Figure 4. These negative charges must be compensated by positively charged ions, which most commonly are H$^+$, Na$^+$, K$^+$, or NH$_4^+$, but other metal ions are also possible. H$^+$ ions in such a framework have strong acidic properties. These charge compensating ions can be easily exchanged, giving the zeolite its ion-exchange capability. In a Cu-CHA, the negative charges are compensated by Cu-ions, and these Cu ions are responsible for the activity of these materials for the NH$_3$-SCR reaction [13,16–25].

The most common oxidation state of Cu is Cu$^{2+}$, and this allows for two fundamentally different configurations for compensation of the negative framework charge. In the first configuration, the Cu$^{2+}$ ion balances the charge induced by a single framework Al ion, by forming a Cu$^{2+}$-OH species at the ion-exchange site, denoted as Z-CuOH. In the second configuration, a single Cu$^{2+}$ ion balances two negative charges simultaneously, which are induced by framework Al sites in the vicinity of each other. This state is denoted as Z$_2$-Cu. It is noted that the actual Cu species in the CHA zeolite is highly dependent on the conditions it is exposed to, including the combination of temperature and NH$_3$-, O$_2$- and H$_2$O concentration [19,26–33].

In the NH$_3$-SCR reaction, the Cu in the CHA zeolite undergoes a redox cycle between Cu$^I$ and Cu$^{II}$ [16,18,20,34]. The reduction of Cu occurs in a reaction with NO and NH$_3$, which leads to the
formation of a mobile $[\text{Cu(NH}_3\text{)}_2]^+$ species at low temperatures \cite{17–20,25,27,33,35} or a Cu$^+$ species at higher temperatures. In the oxidation part, O$_2$ dissociation occurs under the influence of NO, and the Cu is re-oxidized to form Cu$^{II}$-(N,O) species \cite{16,18,20,36,37}.

The catalytic activity of Cu-CHA catalysts in the NH$_3$-SCR reaction can be divided into a low-temperature region (180-300 °C) and a high-temperature region (>350 °C). These are separated by a temperature interval from 300-350 °C where the activity actually drops with increasing temperature, see Figure 5. The advantageous low-temperature activity of these materials are linked to the chemical properties of Cu in these materials. The current understanding of the low-temperature activity of Cu-CHA catalysts is that the O$_2$ dissociation takes place on Cu pairs. The formation of Cu pairs is facilitated by the mobility of the $[\text{Cu(NH}_3\text{)}_2]^+$ species \cite{18,20}. Whether there is an impact of the Cu originating from a Z-CuOH or Z$_Z$-Cu site on the stability or mobility of the $[\text{Cu(NH}_3\text{)}_2]^+$ species is not clear. At higher temperatures, the mobile $[\text{Cu(NH}_3\text{)}_2]^+$ species is not stable and Cu pair formation becomes more difficult, which can result in a lower activity with increasing temperature \cite{20}.

The expected lifetime of an NH$_3$-SCR catalyst in a heavy-duty vehicle is 700000 km, which corresponds to about 10000 h of operation \cite{2}. The catalyst has to be robust enough to maintain a certain level of activity throughout this period. A reason for the great interest in Cu-CHA catalysts is their robustness, which is largely related to the small-pore structure of the CHA zeolite. Thus, the small-pore structure of Cu-CHA catalysts has a significantly better hydrothermal stability than larger pore zeolite structures \cite{38,39}, and are therefore better suited for application in exhaust gas aftertreatment systems. Additionally, diffusion of unburned hydrocarbons into the pores of the zeolite is more difficult in small-pore zeolites, resulting in a better resistance towards deactivation by hydrocarbons as well \cite{8}. The hydrolytic stability has proved to be an issue for SAPO-34 materials, which is a consequence of its more polarized framework \cite{40,41}. The issue with the hydrolytic stability is easily solved by the use of its structural twin, the SSZ-13. However, there are some challenges with the use of Cu-CHA catalysts that are related to their low resistance towards deactivation by SO$_2$.

In EU and USA, ultra-low sulfur diesel (ULSD) is used in order to limit the emissions of SO$_2$. SO$_2$ is not removed in the aftertreatment system, but instead the sulfur content in diesel fuels is regulated. In ULSD, the sulfur content is restricted to a maximum of 10 wt ppm in EU \cite{3}, and 15 wt ppm in USA \cite{2}. The use of ULSD results in approx. 0.5-2 ppmv SO$_2$ in the exhaust gas leaving the engine \cite{2}. Even at these low concentrations of SO$_2$, the low-temperature activity of Cu-CHA catalysts is negatively affected. This is demonstrated in Figure 5, which shows the NO conversion of a Cu-CHA catalyst before and after exposure to SO$_2$. Since the low-temperature activity of Cu-CHA catalysts is one of their main advantages, and this advantage is removed in the presence of exhaust levels of SO$_2$, the susceptibility towards deactivation by SO$_2$ remains an important challenge for the application of Cu-CHA catalysts in diesel exhaust aftertreatment systems.
At the outset of this project, the deactivation of Cu-CHA catalysts by SO\textsubscript{2} was suggested to be a result of ammonium sulfate and copper sulfate [43,44], which implies an oxidation of SO\textsubscript{2}, but the deactivation mechanism was not known. In terms of the deactivation mechanism for ammonium sulfate, it could be envisioned that extensive depositions in the zeolite pores would lead to a limited accessibility of reactants and products to and from the Cu sites. Thus, a pore-blocking deactivation mechanism would be plausible for the deactivation by ammonium sulfates. For copper sulfate, it implies a more direct interaction between the sulfur species and the Cu sites. In that case, it is plausible that the deactivation occurs via a site-blocking mechanism where the redox properties, or the mobility, of the Cu sites are affected by SO\textsubscript{x}.

An improved understanding of the deactivation mechanism(s) could enable new ways of enhancing the resistance of Cu-CHA catalysts towards SO\textsubscript{2}-poisoning, and better assessment of the impact on the SCR performance. The approaches in this work to elucidate this includes investigations with ICP-OES (Inductively-Coupled Plasma – Optical Emission Spectroscopy), TGA (Thermo-Gravimetric Analysis), and SO\textsubscript{2} adsorption/desorption measurements to determine the amounts of sulfur that is captured by Cu-CHA catalysts, and the rate of the sulfur uptake. Furthermore, spectroscopic methods such as EPR (Electron Paramagnetic Spectroscopy) and STEM-EDX (Scanning Transmission Electron Microscopy – Energy Dispersive X-ray) spectroscopy have been used to detect where sulfur is located in the catalyst, and Density Functional Theory calculations have been used to evaluate possible Cu,S structures. Most extensively, kinetic measurements of Cu-CHA catalyst powders in the NH\textsubscript{3}-SCR reaction have been carried out in parallel to all the characterization investigations in order to determine the impact of the sulfur content and the presence of SO\textsubscript{3} on the catalytic performance of the catalyst. Additionally, the impact of temperature and different gas compositions on the sulfation and regeneration processes has been evaluated in micro-reactor scale and monolith-reactor scale.
Objectives

If the deactivation mechanism by SO\textsubscript{2} can be better understood, measures to limit or prevent the deactivation of Cu-CHA catalysts may be developed, and the impact over the catalyst lifetime can be more accurately assessed. This could improve the efficiency of NO\textsubscript{x} removal from heavy-duty diesel vehicle exhaust. The primary focus of this work is, therefore, to develop a solid fundamental understanding of the deactivation behavior of Cu-CHA catalysts by SO\textsubscript{2}, and to assess if the presence of SO\textsubscript{2} in diesel exhaust is prohibitive for practical application of these catalysts in aftertreatment systems of heavy-duty diesel vehicles. These aspects of the work are presented in the different chapters of this thesis.

In Chapter 2, the effect of SO\textsubscript{2} concentration and exposure time on the deactivation of a Cu-SAPO-34 catalysts is established. Furthermore, the influence of NO+NH\textsubscript{3} on the sulfation process is elaborated, and particularly, the possible deactivation mechanisms by ammonium sulfate or copper sulfate are discussed. This is the only chapter where Cu-SAPO-34 has been used, but the role of the chemical composition of the CHA framework with respect to SO\textsubscript{2}-poisoning is shown to be of limited importance.

Chapter 3 focuses on the impacts of temperature, H\textsubscript{2}O, SO\textsubscript{2} and SO\textsubscript{3} on the deactivation of Cu-CHA catalysts. In this chapter, the terms reversible- and irreversible deactivation are introduced and defined, and the different impacts of these on the NH\textsubscript{3}-SCR reaction mechanism are first observed and discussed.

Chapter 4 addresses the distribution of sulfur in the zeolite crystals of an SO\textsubscript{2} exposed Cu-CHA catalyst using scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDX).

The impact of SO\textsubscript{2} over the lifetime of a Cu-CHA catalyst is studied in Chapter 5, where the deactivation after long-term SO\textsubscript{2} exposures at 200, 300, 400, and 500 °C, and subsequent regeneration at 550 °C, are evaluated. In this chapter, the kinetics for formation of sulfate species is touched upon by comparing mass uptakes in TGA experiments to S/Cu ratios determined by ICP-OES. Furthermore, the apparent dependence of the irreversible S/Cu ratio on the Si/Al ratio of the Cu-CHA is elucidated.

A more detailed mechanistic investigation and discussion of the deactivation by SO\textsubscript{2} in relation to the current understanding of the NH\textsubscript{3}-SCR mechanism over Cu-CHA catalysts is described in Chapter 6. This is enabled by exploiting the ability of EPR to observe specific Cu sites in the Cu-CHA catalyst to monitor the development of these sites at increasingly extensive SO\textsubscript{2} exposures in combination with ICP-OES measurements and catalytic performance in the NH\textsubscript{3}-SCR reaction.

A recurring challenge for the investigations of SO\textsubscript{2}-poisoning of Cu-CHA catalysts, and Cu-CHA catalysts in general, is the measurement of active Cu sites. Chapter 7 contains a description of a newly developed method (NO-TPR) to quantify the number of active sites in Cu-CHA catalysts by measuring the consumption of NO during a temperature-programmed reduction of Cu-CHA.
catalysts in NO+NH\textsubscript{3}. The applicability of this method is explored on certain SO\textsubscript{2} exposed, and regenerated, Cu-CHA catalysts.

Finally, Chapter 8 summarizes the conclusions from each chapter into a combined understanding of how SO\textsubscript{2} deactivates Cu-CHA catalysts, and describes the implications of using these catalysts in current and future aftertreatment systems of heavy-duty diesel vehicles.

References


Chapter 1


Chapter 1
Chapter 2

Importance of the Cu oxidation state for the SO$_2$-poisoning of a Cu-SAPO-34 catalyst in the NH$_3$-SCR reaction

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Importance of the Cu oxidation state for the SO$_2$-poisoning of a Cu-SAPO-34 catalyst in the NH$_3$-SCR reaction

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ABSTRACT
Cu-exchanged zeolites of the CHA structure are state-of-the-art catalysts for selective catalytic reduction of NO$_x$ with NH$_3$ in diesel aftertreatment systems. However, these catalysts deactivate in the presence of SO$_2$, which is a constituent of diesel exhaust gas. In this article, the deactivation behavior and mechanisms of a Cu-SAPO-34 catalyst were studied with reactor tests and DFT calculations. Exposure of the catalyst to two different SO$_2$ concentrations and durations, but with the same total SO$_2$ exposure, calculated as the product of partial pressure of SO$_2$ and exposure time, lead to the same degree of deactivation. Exposure of the Cu-SAPO-34 catalyst to SO$_2$ in the presence and absence of NO and NH$_3$ at different temperatures between 200–600 °C showed different trends for the deactivation. Below 400 °C, the S/Cu ratio on the catalyst increased with temperature in absence of NO and NH$_3$, while it decreased with increasing temperature in the presence of NO and NH$_3$. This is explained by the ability of NO and NH$_3$ to reduce Cu(II) to Cu(I). DFT calculations show that SO$_2$ adsorbs more strongly on Cu(I) than on Cu(II). Above 400 °C, the S/Cu ratio decreased with temperature irrespective of the presence of NO and NH$_3$. In all cases, the S/Cu ratio is lower than 1. This is not compatible with extensive deposition of ammonium sulfate when co-feeding SO$_2$, H$_2$O, and NH$_3$. A more likely explanation for the deactivation is that SO$_2$ is mainly related to the Cu sites. This is further corroborated by DFT calculations showing that SO$_2$ and SO$_3$, which is possibly formed by oxidation of SO$_2$ over Cu sites, interact similar with Cu in Cu-SAPO-34 and Cu-SSZ-13.

1. Introduction

Diesel engines operate with excess air in the combustion, leading to production of nitrogen oxides (NO$_x$). NO$_x$ emissions from diesel engines are a source of air pollution and are therefore regulated. To meet legislation requirements for NO$_x$ emissions, a modern aftertreatment systems for diesel engines contain one or more catalysts for the reduction of NO$_x$ to N$_2$. However, these catalysts deactivate in the presence of SO$_2$, which is a constituent of diesel exhaust gas. In this article, the deactivation behavior and mechanisms of a Cu-SAPO-34 catalyst were studied with reactor tests and DFT calculations. Exposure of the catalyst to two different SO$_2$ concentrations and durations, but with the same total SO$_2$ exposure, calculated as the product of partial pressure of SO$_2$ and exposure time, lead to the same degree of deactivation. Exposure of the Cu-SAPO-34 catalyst to SO$_2$ in the presence and absence of NO and NH$_3$ at different temperatures between 200–600 °C showed different trends for the deactivation. Below 400 °C, the S/Cu ratio on the catalyst increased with temperature in absence of NO and NH$_3$, while it decreased with increasing temperature in the presence of NO and NH$_3$. This is explained by the ability of NO and NH$_3$ to reduce Cu(II) to Cu(I). DFT calculations show that SO$_2$ adsorbs more strongly on Cu(I) than on Cu(II). Above 400 °C, the S/Cu ratio decreased with temperature irrespective of the presence of NO and NH$_3$. In all cases, the S/Cu ratio is lower than 1. This is not compatible with extensive deposition of ammonium sulfate when co-feeding SO$_2$, H$_2$O, and NH$_3$. A more likely explanation for the deactivation is that SO$_2$ is mainly related to the Cu sites. This is further corroborated by DFT calculations showing that SO$_2$ and SO$_3$, which is possibly formed by oxidation of SO$_2$ over Cu sites, interact similar with Cu in Cu-SAPO-34 and Cu-SSZ-13.
interaction of SO2 with the Cu-CHA catalyst. Several SO2-poisoning studies have been carried out in gas compositions where NO and NH3 are omitted [4–11]. Such experiments have shown that the deactivation is due to SO2 interactions with Cu, which is dependent on the temperature of SO2 exposure. Adsorption of SO2 mainly takes place at temperatures around 200 °C [5], while chemical reactions between SO2 and Cu become more dominating at temperatures around 400 °C [5]. SO2 reacts at the Cu sites in the CHA, resulting in (Cu,S) species with S in oxidation state +6, which are assigned to isolated Cu-sulfates [4,12]. This assignment is corroborated by their decomposition temperature of around 650 °C, which is consistent with the decomposition of bulk Cu2(SO4) [4,13,14], and by an observed 1:1 correlation between the S/Cu ratio of these species and the deactivation [11]. The formation of sulfates implies that SO2 is oxidized over the catalyst, and the rate of oxidation increases with temperature [10]. The effect of the gas composition on the deactivation by SO2 is not fully understood, and therefore, it is important to improve the understanding in order to be able to transfer results to the SO2-poisoning occurring in real exhausts.

It has been argued that the effect of NO and NH3 on SO2-poisoning is the formation of ammonium sulfate, which may infer mass transfer limitations by pore-blocking [14–16]. However, ammonium sulfate decomposes at about 350 °C, and can therefore feasibly be removed [16]. Moreover, the presence of NO and NH3, or release of NH3 from ammonium sulfate, has suggested a beneficial effect on the regeneration of SO2-poisoned catalysts, due to the reducing properties of the SCR gas mixture and NH3 [8,16].

In this article the SO2 deactivation behavior of a Cu-PAPO-34 catalyst was investigated. The Cu-PAPO-34 was chosen because of its high hydrothermal stability so that high-temperature regeneration did not result in deterioration of the zeolite structure; something that cannot always be avoided with SSZ-13. We investigated the effect of SO2 exposure time, SO2 concentration, and the presence of NO and NH3 on the deactivation by SO2. DFT calculations were used to evaluate the interactions between Cu, SO2, and NH3, in order to obtain a better understanding of the temperature dependence, and effect of NO and NH3, on the deactivation.

2. Experimental

2.1. Catalyst material and reactor testing conditions

In this study, we used a Cu-PAPO-34 catalyst with a (P+Al)/Si of 6.5 and a Cu loading of 1.9 wt%, as determined by ICP-OES. The SCR-feed gas for the activity measurements consisted of 500 ppmv NO, 530 ppmv NH3, 10% O2 and 5% H2O, in N2 at a total flow of 225 N mL/min. The inlet and outlet gas composition was determined using a Gasmet CX4000 FTIR analyser. Prior to the NH3-SCR activity measurements, the catalyst was heated for 1 h in the SCR-feed gas at 550 °C. The effect of SO2 on the NH3-SCR activity was determined from a comparison of the NOx conversion before and after exposure of the catalyst to an SO2-containing feed gas in the same reactor setup.

The catalyst was exposed to SO2 in a flow with either SCR-feed gas, or with 10% O2 and 5% H2O, balanced by N2, to a total flow rate of 225 N mL/min. The inlet concentrations of SO2 were 1.5 or 15 ppmv. The temperature and duration of SO2 exposure were varied and are stated specifically with the results.

The evaluation of the NH3-SCR activity is based on the rate constant of the NH3-SCR reaction. The rate constants (k) are derived from measured steady state NOX conversions, as shown in Eq. (1), assuming plug flow of the gas and that the NH3-SCR reaction is first order in NO.

\[
k = \frac{F}{W} \ln(1-X)
\]

\[F \text{ is the total molar flow rate, } W \text{ is the total mass of catalyst on a dry matter basis, and } X \text{ is the NOx conversion.}
\]

The deactivation of the catalyst is calculated from a comparison of rate constants after SO2 exposure or regeneration with the corresponding rate constant of the fresh catalyst. In this article, we define the deactivation as:

\[
\text{Deactivation} = 1 - \frac{k_{\text{fresh}}}{k}
\]

(2)

2.2. Computational

Spin polarized Density Functional Theory (DFT) calculations were used to obtain adsorption energies of O2, SO2, and SO3 on Cu species in SAPO-34 and SSZ-13. The calculations were performed with the GPAW package [17,18] using a real space grid-based projector augmented wave method. A grid spacing of h = 0.2 Å and a Fermi smearing of 0.1 K were found sufficient to obtain a satisfactory convergence of the relative energies. To account for Van der Waals interactions the BEEF-vdw functional was used [19]. This functional has shown to produce reliable results for the interaction of molecules with zeolites [20,21].

Both SSZ-13 and SAPO-34 were represented by periodic cells with hexagonal symmetry containing 36 T-atoms (SSZ-13 cell parameters: a/b = 13.886 Å, c = 15.116 Å, α = 120°, β = γ = 90° and SAPO-34 cell parameters: a/b = 14.602 Å, c = 15.287 Å, α = 120°, β = γ = 90°).

3. Results

3.1. Deactivation by SO2 exposure and scalability

Fig. 1A shows the measured steady state NOx conversions for the fresh catalyst, after exposure to SO2, and after regeneration at 550 °C. For the SO2 exposure, 1.5 ppmv of SO2 was added to the SCR-feed, which is in the SO2 concentration range expected in automotive diesel exhaust, and the catalyst was held at 300 °C for 8 h. The regeneration of the catalyst was performed at 550 °C for 1 h in SCR-feed gas without SO2. Exposure to SO2 leads to significantly lower steady state NOx conversions in the temperature range 150–300 °C. Regeneration at 550 °C restores most of the original NOx conversion in this temperature range. This behavior has also been observed for an aluminosilicate Cu-CHA catalyst, and can be understood in terms of irreversible and reversible deactivation [11]. According to the definitions in [11], the deactivation measured after regeneration at 550 °C is the irreversible deactivation, and the difference in deactivation after SO2 exposure and regeneration at 550 °C is the reversible deactivation.

For practical reasons when investigating SO2 deactivation, it is often useful to accelerate the SO2-poisoning by increasing the SO2 concentration and proportionally shortening the exposure time. The results are then interpreted in terms of the total SO2 exposure, calculated as the product of the SO2 partial pressure and the exposure time, rather than the SO2 concentration. This interpretation requires that a direct proportionality exists between the exposure time and SO2 concentration, such that these two parameters can be scaled with respect to SO2-poisoning. This scalability was investigated by comparing the results of the non-accelerated SO2 exposure, i.e. exposure to 1.5 ppmv SO2, to the results from a catalyst exposed to an accelerated SO2 exposure. For the accelerated SO2 exposure, the SO2 concentration was increased by a factor 10 and the exposure time was correspondingly decreased, thus exposing to 15 ppmv SO2 in SCR-feed gas for 48 min at 300 °C. The steady state NOx conversions before and after the accelerated SO2 exposure, and after 1 h regeneration at 550 °C in SCR-feed gas, are plotted in Fig. 1B.

The appearance of the NOx conversion curve for the accelerated SO2 exposed catalyst in Fig. 1B, is very similar to that shown in Fig. 1A. The NOx conversions of the fresh catalyst shown in Fig. 1B are slightly lower than those of the fresh catalyst in Fig. 1A, which is due to small
differences in the catalyst loads. Therefore, in order to further confirm
the similarity of the impact of the accelerated and non-accelerated SO2
exposure conditions on the SCR performance of the catalyst, the deac-
tivation (evaluated at 180 °C) after SO2 exposure and regeneration are
plotted in Fig. 1C. The degree of deactivation after both treatments are
similar, with total deactivations of 80 and 79% and irreversible deacti-
vations of 16 and 18%. This means that the deactivation is the same
for the same total SO2 exposure, and indicates that the SO2 concen-
tration and exposure time are scalable.

3.2. Regeneration of the irreversible deactivation

A possible explanation for the irreversible deactivation is the for-
mation of Cu-sulfates that are stable up to ∼650 °C [4,11,13]. If this is
true, a full restoration of the activity of the catalyst by heating to 700 °C
should be possible. This was verified by measuring the SCR activity
over the Cu-zeolite catalyst after SO2 exposure and again after re-
generation at 550 °C and 700 °C. Fig. 2 shows that at 180 °C, the SCR
reaction rate constant is lowest for the sulfated state of the catalyst, and
that regeneration first at 550 °C, partially restores the activity, while
subsequent regeneration at 700 °C restores the activity to the original
level of the fresh catalyst. This result is consistent with Cu-sulfate
species causing the irreversible deactivation, since heating to 700 °C,
which is above the decomposition temperature of CuSO4, restores the
activity of the catalyst completely.

3.3. SO2 exposure in presence of NO and NH3

The SCR catalyst in a diesel exhaust system is exposed to a wide
ranges of temperatures up to approx. 550 °C, with typical operating
temperatures between 200–500 °C. Therefore, the impact of tempera-
ture on the deactivation was investigated by exposing the Cu-zeolite
 catalyst to 1.5 ppmv SO2 for 8 h in the presence of SCR-feed gas at 200,
300, 400 and 500 °C. The measured steady state NOx conversions are
shown in Fig. 3A–D before and after SO2 exposure, and after 1 h of
regeneration at 550 °C in SCR-feed gas. The NOx conversion below
325 °C is lower than for the fresh catalyst in all measurements, for both
the sulfated and regenerated states of the catalyst. Furthermore, the
deactivations in Fig. 4B show that there is a clear trend of more ex-


![Fig. 1. (A) NOx conversion as function of temperature for the Cu-zeolite catalyst before and after exposure to 1.5 ppmv SO2 for 8 h at 300 °C, and after 1 h
regeneration at 550 °C. (B) NOx conversion as function of temperature for the Cu-zeolite catalyst before and after exposure to 15 ppmv SO2 for 48 min at 300 °C,
and after 1 h regeneration at 550 °C. Gas flow conditions for NOx measurements and regenerations were 500 ppmv NO, 530 ppmv NH3, 10% O2, and 5% H2O in N2 at
225 NmL/min. The same gas flow conditions, with addition of SO2, were used for SO2 exposures. (C) Deactivation of the sulfated (blue bars) and regenerated (red
bars) states of the Cu-zeolite catalyst evaluated at 180 °C, after exposure to 1.5 ppmv SO2 for 8 h and 15 ppmv SO2 for 48 min (For interpretation of the references
to color in this figure legend, the reader is referred to the web version of this article).](image_url)

![Fig. 2. The NH3-SCR rate constants of the different states of the Cu-zeolite catalyst, i.e. fresh, sulfated, regenerated at 550 °C, and regenerated at 700 °C.
Sulfation was 24 h at 550 °C in 15 ppmv SO2, 500 ppmv NO, 530 ppmv NH3, 10% O2, and 5% H2O in N2 at 225 NmL/min. The regenerations were 1 h at
550 °C and 2 h at 700 °C, and were carried out with the same flow conditions as the sulfation, but in absence of SO2.](image_url)
exposure temperature are. In the presence of NO and NH₃, the S/Cu ratio decreases monotonically at increased temperature, whereas a maximum for the S/Cu ratio is observed at 400 °C in the absence of NO and NH₃. A possible explanation for the different trends below 400 °C is the deposition of ammonium sulfates in the zeolite pores at low temperatures, which decompose above 350 °C to restore catalytic activity [14–16]. Interestingly, the trends of the S/Cu ratios in the presence and absence of NO and NH₃ appear similar above 400 °C. These results indicate that above 400 °C, the SO₂ exposure conditions are similar despite the different inlet gas compositions. This may be rationalized by the faster SCR reaction rate at higher temperatures, where NO and NH₃ are converted to N₂ and H₂O faster, which means that increasing parts of the catalyst bed are effectively exposed to SO₂ in absence of NO and NH₃ at higher temperatures.

3.4. Stability of reaction products of Cu sites with SO₂ and SO₃

DFT calculations have been carried out to obtain information about the stability of possible SOₓ species that can be formed in reactions between different Cu sites in the Cu-SAPO-34 catalyst and SO₂. Because we cannot exclude the formation of some SO₃ when exposing to SO₂ only, especially at higher temperatures, reactions between Cu sites and SO₃ have also been considered in the calculations. The Cu species that are present in the catalyst is determined by the conditions of the SO₂ exposure. In presence of NO and NH₃, Cu(II) can reduce to Cu(I) [22–26], which is modelled as a naked Cu(I) atom charge-balancing a single exchange site, Z-Cu(I). In presence of O₂ and H₂O, only Cu(II) is expected to be present, which can be in two different forms. Either as a single Cu(II) atom charge-balancing two exchange sites, Z₂-Cu(II), or as...
a Cu(II) atom with a hydroxide ion charge-balancing a single exchange site, Z-Cu(II)OH. The most stable reaction products from reactions between the three different Cu sites with SO$_2$ or SO$_3$, as determined from DFT calculations, are listed in Table 1.

The DFT calculations show that both SO$_2$ and SO$_3$ are able to form stable species with Z-Cu(II)OH and with Z-Cu(I), in agreement with previous DFT calculations [13]. The calculated change in energy for adsorption of SO$_2$, SO$_3$ and O$_2$ on Z$_2$-Cu(II) is positive, indicating that neither of these species adsorb on the Z$_2$-Cu(II) sites. Interestingly, the most stable reaction product of the Z-Cu(I) site is in reaction with SO$_2$, while the Z-Cu(II)OH site forms the most stable species in reaction with SO$_3$. Fig. 7 shows the calculated structures of the resulting Cu species. DFT calculations also indicate that neither SO$_2$ nor SO$_3$ bind to the mobile [Cu(NH$_3$)$_2$]$^+$ species, which provides the active centers for adsorption of SO$_2$, SO$_3$ and O$_2$ on Z$_2$-Cu(II) is positive, indicating that the deactivation by SO$_2$ is determined by the total exposure to SO$_2$.

The data in Fig. 6 show that exposure to SO$_2$ at 200–600 °C results in different amounts of S-uptake by the Cu-SAPO-34 catalyst, dependent on the presence of NO and NH$_3$. These differences can be related to the different amounts of Cu(I) and Cu(II) and the formation of SO$_3$. The DFT calculations presented in Table 1 show that SO$_2$ adsorbs more strongly than SO$_3$ on Z-Cu(I) sites. Since a mixture of NO and NH$_3$ has reducing properties [22–26], the presence of NO and NH$_3$ leads to a larger fraction of Z-Cu(I) species. This leads to an enhanced driving force for SO$_2$ adsorption on Cu in the presence of NO and NH$_3$. The fraction of Z-Cu(I) species decreases with increasing temperature, as a faster SCR reaction leads to lower partial pressures of NO and NH$_3$ and faster re-oxidation of the Cu, and therefore the SO$_2$ uptake decreases with increasing temperature in the presence of NO and NH$_3$, as shown in Fig. 6.

In the absence of NO and NH$_3$, more Cu is present as Cu(II) species, and therefore, the adsorption of SO$_2$ on Cu(II) becomes less important. The DFT calculations show that the Z-Cu(II)OH site forms the most stable CuSO$_x$ species in reaction with SO$_3$, while neither SO$_2$ nor SO$_3$ adsorb on the Z$_2$-Cu(II) sites. Due to the larger amount of Cu(II), the SO$_2$ uptake is now determined by the formation of SO$_3$, which then reacts with the Z-Cu(II)OH sites. The increasing SO$_3$ uptake with temperature in the range 200–400 °C is then a consequence of the increased rate of SO$_2$ oxidation [10]. Above 400 °C, decomposition and desorption of the CuSO$_x$ species takes place [11], resulting in the lower SO$_2$ uptake with increasing temperature.

It is noted that both in the presence and in the absence of NO and NH$_3$, the adsorption of SO$_2$ or SO$_3$ always occurs on Cu sites. Therefore, the total SO$_2$ uptake is limited by the Cu content, in agreement with the observation that the S/Cu ratio does not exceed 1, despite excessive exposure to SO$_2$ (total exposure of SO$_2$/Cu is at least 4.8). It has been

**Table 1**

<table>
<thead>
<tr>
<th>Cu site</th>
<th>$+$ SO$_2$ $\rightarrow$</th>
<th>$\Delta \text{[eV]}$</th>
<th>Cu-SAPO-34</th>
<th>Cu-SSZ-13</th>
<th>$+$ SO$_3$ $\rightarrow$</th>
<th>$\Delta \text{[eV]}$</th>
<th>Cu-SAPO-34</th>
<th>Cu-SSZ-13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-Cu(I)</td>
<td>Z-Cu(I)-SO$_2$ (ads)</td>
<td>$-1.07$</td>
<td>$-1.12$</td>
<td>Z-Cu(I)-SO$_3$ (ads)</td>
<td>$-0.80$</td>
<td>$-0.89$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z-Cu(II)OH</td>
<td>Z-Cu(II)-HSO$_3$</td>
<td>$-0.84$</td>
<td>$-0.73$</td>
<td>Z-Cu(II)-HSO$_3$</td>
<td>$-1.80$</td>
<td>$-1.81$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z$_2$-Cu(II)$^{*}$</td>
<td>O$_2$, SO$_2$, and SO$_3$ do not adsorb on this site in neither Cu-SAPO-34 nor Cu-SSZ-13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The stabilities ($\Delta E$) of most stable reaction products from reactions of three different Cu sites in Cu-SAPO-34 or Cu-SSZ-13 with either SO$_2$ or SO$_3$. *O$_2$ does not adsorb on Z$_2$-Cu(II) in neither Cu-SAPO-34 nor Cu-SSZ-13. Adsorption energies and standard deviations have been obtained from DFT using BEEF-vdW.
argued that deposition of ammonium sulfate in the zeolite pores is the cause of deactivation of Cu-CHA catalysts [14–16]. This explanation would be consistent with a larger S-uptake in presence of NO and NH$_3$ below 400 °C, since ammonium sulfate decomposes at around 350 °C [16]. However, if ammonium sulfate is formed, it is also expected that the amount of sulfur deposited in the catalyst is not limited by the Cu content. Since the S-uptake is limited by the Cu content, formation of ammonium sulfate does not seem to be the cause of the larger SO$_2$ uptake and deactivation in the low temperature range in the presence of NO and NH$_3$.

Finally, the chemical nature of the CHA framework (silicoaluminophosphate or aluminosilicate) seems not to have a significant influence on the deactivation by SO$_2$. As argued in the previous section, the deactivation of the silicoaluminophosphate Cu-SAPO-34 catalyst by SO$_2$ is related to the chemistry of Cu, SO$_2$, SO$_3$, and therefore, SO$_2$-poisoning of the two versions of the Cu-CHA catalysts should be comparable. The response of the Cu-SAPO-34 catalyst to SO$_2$ exposure and regeneration at 550 °C in Fig. 1, is very similar to that observed on a similar aluminosilicate Cu-CHA catalyst [11]. Furthermore, the results from the DFT calculations in Table 1, show that the Cu-SO$_x$ species formed from SO$_2$ and SO$_3$, and the interaction energies of SO$_2$ and SO$_3$ with the respective Cu(I) and Cu(II) species is similar in both CHA materials. This indicates that the framework chemistry of the two Cu-CHA catalysts does not affect the SO$_2$-poisoning, and means that SO$_2$-poisoning is similar on Cu-exchanged aluminosilicate and silicoaluminophosphate CHA materials.

Conclusions

The deactivation behavior of a Cu-SAPO-34 catalyst in the NH$_3$-SCR reaction has been evaluated at simulated operating conditions by comparing the SCR activity before and after exposing to 1.5 ppmv SO$_2$ in a typical SCR-feed gas feed at 300 °C. The low-temperature activity is significantly lowered by the SO$_2$ exposure, and regeneration at 550 °C restores the activity to about 80% of the original level. Regeneration at 700 °C restores all activity, which is consistent with decomposition of Cu-sulfates. The degree of deactivation appears to depend on the total SO$_2$ exposure, calculated as the product of partial pressure and exposure time.

Below 400 °C, the S-uptake increases with temperature in absence of NO and NH$_3$, and decreases with increasing temperature in the presence of NO and NH$_3$. This can be explained by the ability of NO and NH$_3$ to reduce Cu(II) to Cu(I). DFT calculations show that SO$_2$ binds preferably to Cu(I), while SO$_3$ binds stronger to Cu(II). This then leads to the higher uptake of SO$_2$ below 400 °C in the presence of NO and NH$_3$, since a larger amount of Cu(I) is present under these conditions. Above 400 °C, the S-uptake decreases with increasing temperature, independent of the presence of NO and NH$_3$.

The S/Cu ratios are always lower than 1, which indicates that the uptake of sulfur is related to adsorption of SO$_2$ on Cu and that ammonium sulfate does not precipitate in the catalyst when co-feeding SO$_2$, NO, and NH$_3$. Furthermore, DFT calculations also show that SO$_2$ and SO$_3$ interactions with Cu is similar for Cu-SAPO-34 and Cu-SSZ-13, indicating that the deactivation by SO$_2$ is mainly associated to the chemistry of the Cu sites. Consequently, the SO$_2$-poisoning mechanisms for Cu-SAPO-34 and Cu-SSZ-13 are comparable.

Acknowledgement

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References


[7] K. Wijayanti, S. Andonova, A. Kumar, J. Li, K. Kamasamudram, N.W. Currier, A. Yezerets, Chemical nature of the CHA framework (silicoaluminophosphate or aluminosilicate) seems not to have a significant influence on the deactivation by SO$_2$. As argued in the previous section, the deactivation of the silicoaluminophosphate Cu-SAPO-34 catalyst by SO$_2$ is related to the chemistry of Cu, SO$_2$, SO$_3$, and therefore, SO$_2$-poisoning of the two versions of the Cu-CHA catalysts should be comparable. The response of the Cu-SAPO-34 catalyst to SO$_2$ exposure and regeneration at 550 °C in Fig. 1, is very similar to that observed on a similar aluminosilicate Cu-CHA catalyst [11]. Furthermore, the results from the DFT calculations in Table 1, show that the Cu-SO$_x$ species formed from SO$_2$ and SO$_3$, and the interaction energies of SO$_2$ and SO$_3$ with the respective Cu(I) and Cu(II) species is similar in both CHA materials. This indicates that the framework chemistry of the two Cu-CHA catalysts does not affect the SO$_2$-poisoning, and means that SO$_2$-poisoning is similar on Cu-exchanged aluminosilicate and silicoaluminophosphate CHA materials.

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Chapter 2

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Chapter 3

Reversible and irreversible deactivation of Cu-CHA NH$_3$-SCR catalysts by SO$_2$ and SO$_3$

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Reversible and irreversible deactivation of Cu-CHA NH₃-SCR catalysts by SO₂ and SO₃

Peter S. Hammershøi, Yasser Jangjou, William S. Epling, Anker D. Jensen, Ton V.W. Janssens

Keywords: NH₃-SCR, Cu-CHA, Deactivation, Sulfur oxides, Regeneration

ABSTRACT

Sulfur oxides are a common source for the deactivation of Cu-exchanged CHA zeolite based catalysts used for NOx reduction in diesel exhausts by selective catalytic reduction with NH₃ (NH₃-SCR). Since water and possible formation of SO₂ affect the deactivation of Cu-CHA catalysts, the deactivation in the presence of SO₂ or a mixture of SO₂ and SO₃ was studied by measuring the SCR activity in wet and dry gas at 200 and 550 °C. The estimated S-content in the catalysts before and after 4 h regeneration at 550 °C in NO, NH₃, O₂ and H₂O was related to the deactivation. The deactivation can be divided into two parts: a reversible deactivation that is restored by the regeneration treatment, and an irreversible part. The irreversible deactivation does not affect the activation energy for NH₃-SCR and display a 1:1 correlation with the S-content, consistent with deactivation by Cu-sulfate formation. The reversible deactivation results in a lower activation energy and a deactivation that is larger than expected from the S-content. The presence of SO₃ at 200 °C leads to higher reversible and irreversible deactivation, but has no significant impact at 550 °C. Furthermore, the irreversible deactivation is always higher when exposed at 200 °C than at 550 °C, and in wet conditions, compared to a dry feed. The deactivation is predominantly reversible, making regeneration at 550 °C a realistic approach to handle S-poisoning in exhaust systems.

1. Introduction

Combustion of diesel fuel in automotive engines produces NOx (NO and NO₂). Due to the environmentally negative impact of NOx emissions of these compounds are subject to strict regulations, which requires NOx reduction from the exhaust gas. The current technology for the removal of NOx is selective catalytic reduction (SCR) of NOx with NH₃. Apart from an NH₃-SCR catalyst, a complete diesel exhaust after-treatment system also contains a diesel oxidation catalyst to oxidize CO and unburnt fuel, a particle filter to remove soot, and an ammonia slip catalyst to remove the ammonia not used in the upstream NH₃-SCR reaction.

The best known NH₃-SCR catalysts are based on V₂O₅ or Cu- or Fe-zeolites. Compared to V₂O₅-based catalyst systems, Cu-zeolites generally work well in a broader temperature region (~150–500 °C) [1]. In particular, the better low temperature activity for Cu-zeolites is of interest for cold-start conditions. Combined with the good hydrothermal stability of small-pore zeolites, these traits have led to commercialization of Cu-zeolites in diesel engine exhaust systems, and Cu-CHA is the current state-of-the-art Cu-zeolite catalyst for diesel emission control.

Another important requirement for NH₃-SCR catalysts is low susceptibility to SO₂-poisoning. Diesel fuels contain a small amount of sulfur, and even ultra-low sulfur fuel will result in SO₂ in the exhaust gas. The performance of NH₃-SCR catalysts, however, can be very sensitive to the presence of SO₂ even at low concentrations, as in ultra-low sulfur diesel [2]. It is therefore important to know the effect of SO₂ on the performance of an NH₃-SCR catalysts.

Unfortunately, Cu-zeolite catalysts deactivate more in the presence of SO₂ in the exhaust gas, while Fe-zeolites are less affected by SO₂ and V₂O₅ is not affected [1,3,4]. Consequently, to be able to exploit the potentially better performance of Cu-zeolite catalysts in an exhaust after-treatment system, it is important to understand how the presence of SO₂ influences the performance of these catalysts. Furthermore, it is also important to know to what degree the deactivation of Cu-zeolites...
induced by SO₂ is reversible versus irreversible.

The current understanding of Cu-zeolite catalyst deactivation by SO₂, and Cu-CHA in particular, is that it originates from SO₃ interaction with the Cu-sites. This can simply be adsorption of SO₃ or could involve a chemical reaction between the SO₃ and Cu-sites [2,5–13]. X-ray photoemission and X-ray absorption spectroscopy indicate that the Cu in the ion-exchange positions reacts to form a Cu₃S₂O₆-like species [2]. The formation of sulfates suggests that some oxidation of SO₂ to SO₃ takes place. In an after-treatment system, oxidation of SO₂ to SO₃ can occur on the diesel oxidation catalyst [2,11], and on the NH₃-SCR catalyst [5,9,10].

A higher sulfur uptake and stronger deactivation has been observed in the presence of SO₃ in the feed gas [2,11]. Therefore, a better understanding of the effect of SO₃ on the performance of NH₃-SCR catalysts is needed.

Another mechanism for deactivation of NH₃-SCR catalysts is the formation of ammonium sulfate on the catalyst, which restricts access to the active sites. The presence of SO₂ or SO₃ in a standard, NH₃-containing SCR-gas causes formation of ammonium sulfate, which is a solid below 300 °C, and therefore, deactivation by ammonium sulfate only occurs in the low-temperature range. Ammonium sulfate can be removed by heating the catalyst to above 350 °C, which means that regeneration from this type of deactivation is possible in an exhaust system [5,9,10].

An NH₃-SCR catalyst in a diesel exhaust treatment system is typically operated between 200 and 550 °C, and in the presence of 5–10% water vapor. The effect of temperature on catalyst deactivation by SO₃ depends on the presence of SO₂ [2,11]. With SO₂ only, the deactivation is more severe at 200 °C than at 400 °C, while the opposite trend is observed in the presence of SO₃ [2,11].

Water also interacts with the Cu ions, changing the environment of and around the active sites in a Cu-CHA catalyst. Water vapor is known to partially hydrolyze the Cu-sites at temperatures below 250 °C [11], affecting the performance for NH₃-SCR. In a similar way, reactions with sulfur oxides can be affected by water as well [8,15]. From a mechanistic point of view, the impact of water vapor on the deactivation by SO₂ and SO₃ should be understood, with the additional consideration that SO₂ and H₂O combine and form sulfuric acid below 400 °C [11].

In practice, there are essentially two ways to deal with the presence of SO₃ in an exhaust gas. The first one is to design the Cu-CHA SCR catalysts in such a way that the amounts of SO₂ and SO₃ passing through the system during its lifetime can be accommodated in the system. Alternatively, periodic regeneration strategies must be designed that restore at least a part of the catalytic activity. It is therefore important to know how the presence of SO₂ and SO₃ in the exhaust gas stream affects the performance of Cu-CHA catalyst and if regeneration of a Cu-CHA catalyst is possible. In this article, we focus on the effect of the temperature and H₂O and SO₃ on the SO₃-induced deactivation of a monolithic Cu-CHA catalyst for NH₃-SCR. The stability of species formed was studied by comparing the activities of a deactivated catalyst with that after heating to 550 °C, which is a temperature that can be reached in an exhaust system.

2. Experimental

2.1. Preparation of the catalysts

In this study we used both a Cu-CHA powder catalyst and a monolithic Cu-CHA catalyst. For the powdered catalyst, Cu was introduced into the H-CHA zeolite by ion-exchange for 24 h with an aqueous solution of Cu(CH₃COO)₂ (5 mmol/kg) at 20 °C, using 20 g H-CHA zeolite powder in 5 kg solution. After ion-exchange the Cu-CHA was filtered and washed with approx. 20 L MilliQ water, which resulted in a colorless filtrate. The Cu-CHA powder was then dried overnight at 95 °C, and calcined at 550 °C for 3 h. The Si/Al ratio was 14.7 and the Cu/Al ratio was 0.5, corresponding to a Cu-loading of 2.8 wt%, as determined by ICP-OES.

The monolithic Cu-CHA catalyst was prepared by washcoating a cordierite monolith with a slurry of H₂O, xanthan gum, colloidal silica and Cu-CHA powder. The Cu-CHA powder was prepared by impregnating 1 kg of H-CHA powder (Si/Al = 16-6) with Cu in 1 kg of an aqueous solution of 0.39 mmol/g Cu(NO₃)₂·3H₂O in a rotary evaporator for 4 h at 95 °C. The Cu-loading of the powder was 2.5 wt%, based on the amount of Cu added for the impregnation. After impregnation, the powder was calcined at 550 °C for 3 h. A cordierite monolith (D × L = 25.4 × 10.2 cm, 300 cpsi, 0.13 mm wall thickness) was washcoated with the Cu-CHA slurry to a washcoat-loading of 151 g/L. The Cu-CHA/cordierite monolith was dried at 100 °C, and calcined at 550 °C for 3 h.

2.2. Catalytic test on powder

The NH₃-SCR activity measurements on the Cu-CHA powder were carried out in a fixed-bed quartz reactor with a 2 mm inner diameter, using 5.0 mg catalyst (150–300 μm sieve fraction) on a dry matter basis. The SCR feed gas composition was 500 ppm NO, 530 ppm NH₃, 10% O₂, 5% H₂O balanced by N₂, which we hereafter refer to as "SCR-gas". The total flow rate used in the measurements was 0.225 NL/min (10 mmol/min, standard conditions: T = 0 °C, P = 1 atm). The outlet gas was analyzed by a Gasmet CX4000 FTIR analyzer.

The Cu-CHA powder exposure to SO₃ was either done in situ in the reactor at 550 °C for 1 h with 40 ppmv SO₂, 10% O₂, 5% H₂O balanced by N₂ with a total flow rate of 0.2 NL/min (9 mmol/min), or ex situ in a tube furnace at 550 °C for 16 h with 100 ppmv SO₂, 16% O₂, balanced by N₂ with a total flow rate of 0.2 NL/min. Regeneration was always carried out in situ in the reactor at 550 °C with an SCR-gas flow of 0.225 NL/min. 550 °C was chosen, as this is a typical temperature for regeneration of diesel after-treatment systems operating with passive filter regeneration.

2.3. Catalytic test on monoliths

With the purpose of studying the impact of temperature and H₂O and SO₃ gas components on Cu-CHA/cordierite monolith catalyst deactivation by SO₂, steady-state NOx conversions were measured before and after SO₃ exposure, and after regeneration at 550 °C in a laboratory flow reactor system with a horizontal quartz reactor with an inner diameter of 25.4 mm. Upstream and downstream tubing inside surfaces were coated with SilcoNert to minimize adsorption of SO₃ (and NH₃). Monolith samples of approx. 20 × 27 mm were cut out from the larger prepared sample (sample masses were between 4.5–5.0 g). The reactor temperature was measured at the inlet, inside, and at the outlet of the monolith samples by thermocouples placed in the radial center of the reactor/sample. The steady-state NOx conversions were measured at various temperatures (130–250 °C), at a flow of 8.0 NL/min (357 mmol/min). The SCR feed gas composition was 500 ppm NO, 530 ppm NH₃, 10% O₂, 5% H₂O balanced by N₂. The outlet gas was analyzed using a MKS MultiGas 2030 FTIR. SO₃ exposure was always 3 h in 10% O₂ with 100 ppmv SO₃ balanced by N₂ with a total flow rate of 8.0 NL/min. The variations in the SO₃ exposure conditions and the assigned sample names are listed in Table 1. The SO₃ for the SO₃ exposures, was produced in an upstream reactor by oxidizing SO₂ over a Pt/Al₂O₃ monolith catalyst. The temperature of the upstream reactor was adjusted to reach a steady-state conversion of SO₂ of 30%, which was added to the main feed prior to the inlet of the quartz reactor containing the Cu-CHA/cordierite catalyst. Regeneration was carried out in the SCR feed gas at 550 °C, heating at 10 °C/min, for 4 h. In order to check if there were S-species remaining on the samples after regeneration, temperature-programmed desorption (TPD) to 900 °C was carried out after the final NOx conversion measurement that followed the regeneration. The SO₃-TPD was carried out in N₂ at a flow rate of 8.0 NL/min, and with a temperature ramp at 10 °C/min. The
Concentrations of H$_2$O, NO, NO$_2$, NH$_3$, SO$_2$, SO$_3$, and H$_2$SO$_4$ were monitored during regenerations and TPD measurements.

2.4. Evaluation of activity and deactivation

The activities of the catalysts are evaluated by the rate constants, which are derived from the steady-state NO$_x$ conversion measurements. If we assume that the NH$_3$-SCR reaction is first order in NO, the rate constant is given by:

$$k = \frac{F}{W} \ln(1 - X)$$

where $F$ is the total molar flow rate, $W$ is the mass of the Cu-CHA powder in both tested catalysts, and $X$ is the conversion of NO. The deactivation is expressed as the relative rate constant of a sulfated or regenerated catalyst with respect to the rate constant for the fresh catalyst:

$$\text{Deactivation} = 1 - \frac{k}{k_{\text{fresh}}} = 1 - \frac{A \exp\left(-\frac{E_a}{RT}\right)}{A_{\text{fresh}} \exp\left(-\frac{E_a}{RT}\right)}$$

(2)

Multiplication by 100 then yields the deactivation expressed as a percentage.

3. Results

3.1. Powder experiments

The general behavior of a Cu-CHA catalyst upon exposure to SO$_2$ and regeneration at 550 °C is illustrated in Fig. 1 for the powder catalyst, which shows the measured NO$_x$ conversions for a fresh catalyst, after exposure to 100 ppm SO$_2$ at 550 °C (sulfated), and after regeneration at 550 °C in SCR-gas (regenerated).

The most significant effect of exposure to SO$_2$ is seen in the lower temperature range, up to 300 °C, where NO$_x$ conversion was significantly inhibited compared to the fresh sample. Above 300 °C, the NO$_x$ conversion increases rapidly with temperature to slightly above the conversion measured for the fresh catalyst. After regeneration by heating to 550 °C, the conversion above 300 °C was slightly higher, but close to that of the fresh catalyst. Below 300 °C, the conversion remained slightly below that of the fresh catalyst. This shows that exposure to SO$_2$ results mainly in deactivation of the low-temperature (T < 350 °C) activity of the catalyst, which is consistent with previously reported observations [5,9,11], and regeneration at 550 °C does not fully restore the activity below 300 °C entirely.

To investigate if the incomplete regeneration at 550 °C is due to a too short regeneration time, the regeneration process was monitored by heating the samples at 550 °C for a total of 12 h in intervals, where after each interval the activity at 200 °C was re-evaluated. Fig. 2A shows the measured activity at 200 °C obtained in this way, which indicates that a stable activity level is reached at about 75-80% of the original activity after approximately 4 h of regeneration. This means that a complete regeneration by heating at 550 °C seems not possible.

Fig. 1 shows that the NO$_x$ conversion over a catalyst after exposure to SO$_2$ increases slightly with temperature up to 300 °C, followed by a steep increase. To determine whether the slight increase below 300 °C is due to a normal temperature dependency of a possible residual activity, or to a slow regeneration in this temperature range, we checked the influence of the temperature on activity of a Cu-CHA catalyst at 200 °C. To do this measurement, a single catalyst sample deactivated by SO$_2$ was sequentially exposed to heating for 2 h in 5% H$_2$O/10% O$_2$/N$_2$ at a chosen temperature between 200 and 450 °C in increasing order, and then cooled down to 200 °C where the NO$_x$ conversion was then re-measured. Fig. 2B shows the rate constant at 200 °C, determined according to Eq. (1) as a function of the heating constant at 200 °C does not increase by heating to a temperature of 300 °C or lower, which clearly indicates that the regeneration of a catalyst exposed to SO$_2$ does not start below 300 °C, and the slight increase in conversion in Fig. 1 is therefore due to the temperature dependence of a residual activity. This also means that measured SCR activities after exposure to SO$_2$ are not affected by regeneration if the measurements are done at 300 °C or lower.

The observation that the activity after SO$_2$ exposure cannot be completely restored by heating to 550 °C indicates that there are different forms of deactivation. Based on these data, we define these different forms of deactivation as follows: the part of the deactivation that can be restored by 4 h heating at 550 °C will be referred to as the reversible deactivation, and the remaining part as the irreversible deactivation. The total deactivation is the sum of these two contributions. An activity measured after exposure to SO$_2$, before regeneration, represents the total deactivation, the irreversible deactivation is found from the activity after regeneration. The reversible deactivation can then be determined as the difference in activity of a SO$_2$-treated catalyst before and after regeneration. The following expression is used to determine the relative reversible deactivation with respect to the activity of the fresh catalyst:

$$1 - \frac{k_{\text{sulfated}}}{k_{\text{fresh}}} = \text{Reversible deactivation} + \left(1 - \frac{k_{\text{removable}}}{k_{\text{fresh}}}, \right)$$

(3)

3.2. Monolith experiments

The effects of SO$_2$, water, and SO$_x$ exposure temperature on the catalyst deactivation and regeneration was studied by measurement of NO conversions over Cu-CHA/cordierite monolith samples after exposure to SO$_2$ at the conditions listed in Table 1, and after subsequent
heating at 550 °C. In all these measurements, the deactivation and regeneration followed the same general trend as observed for the Cu-CHA powder. Fig. 3 shows the measured NOx conversion in the range 150–250 °C after deactivation in wet SO2 without SO3 as an example. Exposure to SO2 leads to a lower NOx conversion, which is mostly restored by heating at 550 °C. It is noted that all activity measurements shown in Fig. 3 are obtained below 300 °C, and are therefore not influenced by regeneration during the measurements.

Due to variations in temperature in the different measurements, a common base for comparison of the measured NOx conversions is needed. To this end, Arrhenius plots were constructed; Fig. 4 shows the Arrhenius plot based on the data in Fig. 3, and represents the general observation for all samples (see supporting information). For all conditions, the slopes of the fresh and regenerated states of the catalyst are nearly the same, while the slope of the sulfated state of the catalyst is always smaller. Our interpretation is that the activation energies for the fresh and regenerated catalysts are the same, and the activation energy was determined from the combined data points of the fresh and regenerated states. Consequently, the differences in activity for fresh and regenerated catalysts are translated to differences in the pre-exponential factor. The relative irreversible deactivation then becomes independent of the temperature for the conditions used here. The assignment of irreversible deactivation to changes in the pre-exponential factor implies a mechanism in which deactivation is caused by loss of active sites, without major changes in the chemistry of the reaction.

The situation is different for the sulfated catalysts, which consistently have lower activation energy than the fresh and regenerated catalysts. Table 2 lists the activation energies for the fresh and sulfated samples, and the ratio of the two values. The lower activation energies of the sulfated catalysts also mean that the measured reversible deactivation depends on the temperature of the SCR activity measurement. A change in activation energy cannot be due to a loss of active sites only. Phenomena that could change the activation energy are a change in the chemistry of the NH3-SCR reaction and diffusion limitations of the NH3-SCR reaction rate in the zeolite crystals after exposure to SOx.

An option for the samples treated with SO2 alone. For the samples

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$k_{a,\text{air}}$ (mol g$^{-1}$ s$^{-1}$)</th>
<th>$k_{a,\text{air}}/E_a$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2-H2O-200</td>
<td>91 ± 8</td>
<td>38 ± 5</td>
<td>0.33–0.53</td>
</tr>
<tr>
<td>SO2-200</td>
<td>99 ± 3</td>
<td>53 ± 2</td>
<td>0.50–0.58</td>
</tr>
<tr>
<td>SO2-H2O-550</td>
<td>90 ± 7</td>
<td>53 ± 1</td>
<td>0.54–0.65</td>
</tr>
<tr>
<td>SO2-550</td>
<td>59 ± 3</td>
<td>30 ± 5</td>
<td>0.41–0.63</td>
</tr>
<tr>
<td>SO5-H2O-200</td>
<td>80 ± 26</td>
<td>15 ± 2</td>
<td>0.12–0.32</td>
</tr>
<tr>
<td>SO3-200</td>
<td>115 ± 16</td>
<td>39 ± 4</td>
<td>0.27–0.45</td>
</tr>
<tr>
<td>SO3-H2O-550</td>
<td>97 ± 4</td>
<td>39 ± 1</td>
<td>0.38–0.43</td>
</tr>
<tr>
<td>SO3-550</td>
<td>76 ± 5</td>
<td>31 ± 1</td>
<td>0.36–0.45</td>
</tr>
</tbody>
</table>
treated with SO$_3$, the activation energy ratios are lower than 0.5, which cannot be explained by internal diffusion limitations alone, suggesting that chemical effects are more pronounced in this case.

### 3.3. Desorption of SO$_2$

To determine the amount of sulfur deposited on the catalysts, SO$_2$ concentrations were measured during the regeneration up to and at 550°C in SCR-gas, and during heating to 900°C in N$_2$ after all activity measurements. The measured SO$_2$ desorption during the regeneration to 550°C, shown in Fig. 5A, is related to the reversible deactivation. No SO$_2$ or H$_2$SO$_4$ desorption was observed during the regeneration. Clearly, the two samples exposed to SO$_3$ at 200°C stand out with a substantially higher SO$_2$ desorption around 400°C. Since the two catalysts exposed to SO$_3$ at 200°C did not show a similar high SO$_2$ desorption around 400°C, the higher desorption of SO$_2$ from the two catalysts exposed to SO$_3$ at 200°C must be due to decomposition of SO$_3$ or sulfates [2,11,12]. The desorption temperature of 400°C is about 200–250°C lower than the decomposition temperature of bulk Cu-sulfate [12]. This indicates that only little Cu sulfate is formed from SO$_3$ at 200°C, or that the Cu-sulfate species formed this way in the Cu-CHA catalysts are less stable than bulk Cu-sulfate.

All other samples, exposed to SO$_2$ at 200°C or SO$_2$ + SO$_3$ at 550°C, show similar SO$_2$ desorption peaks at approx. 300°C and 475°C. This means that exposure to SO$_3$ at 550°C essentially results in similar sulfur species as exposure to SO$_2$ at 200 or 550°C, and the influence of water is limited. The observed desorption temperatures are consistent with decomposition of ammonium sulfate [5] and sulfuric acid [12,15]. Ammonium sulfates can possibly have been formed by the exposure of the sulfated samples to NH$_3$ during the SCR activity measurement directly after the SO$_3$ exposure [10], which would imply a reaction of the adsorbed sulfur species and ammonia.

Fig. 5B shows the desorption of SO$_3$ during heating in N$_2$ to 900°C after SO$_3$ exposure and regeneration, which represents the sulfur species associated with irreversible deactivation. The catalysts exposed to SO$_3$ at 200°C show again the largest amount of SO$_3$. The desorption peak is centered around 675°C for all samples, indicating that the same species is formed in all catalysts, but in different amounts, dependent on the conditions for SO$_3$ exposure. The temperature of 675°C is consistent with the irreversible deactivation being related to formation of Cu-sulfate [12].

From integration of the curves in Fig. 5, the amounts of sulfur in the sulfated and regenerated catalysts can be estimated, and we highlight the differences in sulfur content between the samples exposed to SO$_3$ at 200°C and the other samples. The quality of the measured SO$_2$ concentrations during regeneration is poor, but the differences between the samples exposed to SO$_3$ at 200°C and the other ones are quite clear. We also note that no SO$_3$ was detected during the temperature programmed desorption, and no sulfur was found in an ICP-OES analysis of the catalysts after heating to 900°C. This means that the amounts of sulfur detected in the desorption measurements accounts for all sulfur present in the catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reversible SO$_2$/Cu</th>
<th>Irreversible SO$_2$/Cu</th>
<th>Total SO$_2$/Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$-H$_2$O-200</td>
<td>0.07</td>
<td>0.09</td>
<td>0.16</td>
</tr>
<tr>
<td>SO$_3$-200</td>
<td>0.04</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>SO$_3$-H$_2$O-550</td>
<td>0.04</td>
<td>0.12</td>
<td>0.16</td>
</tr>
<tr>
<td>SO$_3$-550</td>
<td>0.10</td>
<td>0.02</td>
<td>0.12</td>
</tr>
<tr>
<td>SO$_3$-H$_2$O-200</td>
<td>0.74</td>
<td>0.16</td>
<td>0.90</td>
</tr>
<tr>
<td>SO$_3$-200</td>
<td>0.40</td>
<td>0.18</td>
<td>0.58</td>
</tr>
<tr>
<td>SO$_3$-H$_2$O-550</td>
<td>0.09</td>
<td>0.08</td>
<td>0.17</td>
</tr>
<tr>
<td>SO$_3$-550</td>
<td>0.13</td>
<td>0.03</td>
<td>0.16</td>
</tr>
</tbody>
</table>

### 3.4. Influence of SO$_2$/SO$_3$, water and temperature on deactivation

Having established the general trends in performance and sulfur content after sulfation, and regeneration of the Cu-CHA catalyst, we now turn our attention to the effects of temperature of SO$_3$ exposure, and the presence of water or SO$_3$. Fig. 6A and B shows the reversible and irreversible deactivation for the samples exposed to SO$_2$ only and SO$_2$ + SO$_3$. The reversible deactivation was derived from interpolation of the activity data to 180°C, using the Arrhenius plots given in Fig. 2 and supporting information. The deactivation is given as a percentage according to Eq. (2).

The effect of SO$_3$ on deactivation is most noticeable with SO$_3$ exposure at 200°C, leading to significantly stronger deactivation, compared to exposure to SO$_2$ alone both in dry and wet feed gases. At 550°C, there is no apparent influence of SO$_3$ in the feed gas.
shows that the specific deactivation by SO₃ is most important in the lower temperature range, and that the effect of SO₃ on deactivation is related to the pronounced decomposition of SO₃ or sulfate at 400 °C, as shown in Fig. 5A.

The presence of H₂O during SO₃ exposure always leads to higher irreversible deactivation than the corresponding dry SO₃ exposure condition, but appears to have no consistent influence on reversible deactivation. With respect to the impact of temperature, irreversible deactivation is always greater in the samples exposed at 200 °C than the corresponding sample exposed at 550 °C, whereas no consistent impact of temperature is observed on reversible deactivation. The general picture that emerges is that the presence of SO₃ and water at 200 °C has a stronger effect on the deactivation than at 550 °C, in particular on irreversible deactivation.

4. Discussion

The similar activation energies in the SCR reaction for the fresh and regenerated states of the catalysts indicates that irreversible deactivation is the result of having fewer active sites available, and the desorption temperature for SO₂ from the regenerated catalysts points to the formation of Cu-sulfate. If Cu-sulfate formation is the cause of deactivation, a 1:1 correlation should exist between the irreversible deactivation and the sulfur content. Fig. 7 shows the measured irreversible deactivation as a function of the SO₂/Cu ratio, derived from the corresponding SO₂ desorption measurements in Fig. 5B, together with the line for the 1:1 correlation. The measured irreversible deactivation actually follows the 1:1 correlation with the sulfur content fairly well, corroborating the idea that Cu-sulfate formation is responsible for the irreversible deactivation [2,5–13].

A way to envision the irreversible deactivation by formation of a Cu-sulfate species is a reaction of SO₃ with a Cu-ion balanced by a single Al and a hydroxide ligand (Z-Cu-OH), as in reaction Scheme (4).

\[
Z-\text{Cu} - \text{OH} + \text{SO}_3 \rightarrow Z-\text{Cu} - \text{HSO}_4
\]

In this case, the hydroxide ligand provides the oxygen required for formation of sulfate. A Cu²⁺ ion balanced by two Al-sites (Z₂-Cu) does not have the hydroxide ligand, but this does not necessarily mean that these Cu-species are incapable of sulfate formation. In the presence of water, a Z₂-Cu can react to a Z-Cu-OH and a Brønsted acid site [14], and the Z-Cu-OH can then react further with SO₃ according to reaction Scheme (4). The overall reaction then becomes:

\[
Z_2-\text{Cu} + \text{SO}_3 + \text{H}_2\text{O} \rightarrow Z-\text{Cu} - \text{HSO}_4 + Z-\text{H}
\]

A similar scenario is a reaction with sulfuric acid (H₂SO₄) and a Z₂-Cu site, where the sulfuric acid is formed by reaction of SO₃ and water. Either way, the presence of water would facilitate formation of Cu-sulfate as this leads to a higher amount of Z-Cu-OH-sites compared to dry conditions. The suggested reaction schemes then offer an explanation for the increase in irreversible deactivation in the presence of water. This means that a model that describes the irreversible deactivation by formation of Cu-sulfate is also consistent with the observed effects of the presence of water.

A comparison of measured deactivation and the sulfur content for the sulfated catalysts reveals a different behavior for reversible deactivation. Fig. 8 shows the total deactivation of the sulfated catalysts as a function of their total SO₂/Cu ratios. Clearly, there is no consistent 1:1

![Fig. 6. The reversible deactivation (blue bars), irreversible deactivation (red bars) and total deactivation (sum of red and blue bars) plotted for each SOx exposure condition of the Cu-CHA/cordierite catalysts. A) samples exposed to 100 ppmv SO₂, B) samples exposed to 70 ppmv SO₂ and 30 ppmv SO₃. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
dependence of the total deactivation on SO2/Cu ratio, with only small SO2/Cu ratios, between 10 and 20%, leading to degrees of deactivation which indicates that the reaction in the fresh catalyst is not limited by diffusion of reactants.

The lower activation energies of the sulfated catalysts might be due to formation of internal diffusion limitations induced by SOx deactivation, which can play a role in the deactivation process. In case of increased diffusion limitations, the effectiveness factor should become lower in addition to the loss of sites, resulting in an overall deactivation that is higher than the fraction of Cu sites in contact with sulfur. This agrees, at least qualitatively, with the results shown in Fig. 8. To evaluate a possible effect of diffusion limitations, the effectiveness factor, $\eta$, was calculated for the fresh catalyst, assuming spherical zeolite crystals and first order reaction kinetics in NO. For the calculations, the crystal radius was set to 0.5 μm, which is a reasonable value given that the crystal size of the zeolite is on the order of 1 μm. A further description of the calculation of the effectiveness factor is given in supporting information. Fig. 9 shows the effectiveness factor as a function of the effective diffusion coefficient, $D_{\text{eff}}$, at 180 °C. By extrapolation of experimentally determined values for effective diffusion coefficients for NH3 in a Cu-CHA catalyst in the range 0–100 °C, is marked, which indicates that the reaction in the fresh catalyst is not limited by diffusion of reactants.

Using this data, the effectiveness factor can be expressed as $\eta(D_{\text{eff}} = 1.2 \times 10^{-9} \text{ m}^2/\text{s})$.

Fig. 9. Double logarithmic plot of the internal effectiveness factor in the zeolite crystals, $\eta$, at 180 °C, as a function of the effective diffusion coefficient, $D_{\text{eff}}$. $\eta$ based on experimental values for $D_{\text{eff}}$ of NH3 in a Cu-CHA catalyst in the range 0–100 °C, is marked, which indicates that the reaction in the fresh catalyst is not limited by diffusion of reactants.

$\eta(D_{\text{eff}} = 1.2 \times 10^{-9} \text{ m}^2/\text{s})$

The mechanisms behind the reversible and irreversible deactivation remain unanswered. Having ruled out diffusion as a cause for reversible deactivation, the lower activation energy must then be related to changes in the chemistry. An interesting concept is Cu being able to form a mobile diamine species at SCR conditions. These mobile Cu-diamine species are important for the low-temperature activity of Cu-CHA catalysts [17–20]. Possibly, the reversible deactivation by sulfur oxide species inhibits the formation of these mobile Cu diamine complexes, thereby lowering the mobility of Cu and the NH3-SCR activity, which might lead to the observed high degree of reversible deactivation with low amounts of sulfur.

Finally, our data clearly show that exposure to SOx at lower temperatures result in the largest deactivation. However, most of the catalytic activity can be regained by heating to 550 °C, even after exposure to SOx at 200 °C. This is an interesting result from an application point of view, since it indicates that regeneration strategies based on heating to easily obtainable temperatures in exhaust systems are a feasible solution to handle deactivation of Cu-zeolites by SOx and SO2 [10,13].

5. Conclusion

To evaluate different aspects of sulfur poisoning of NH3-SCR activity, Cu-CHA catalysts were exposed to SO2 or a 70:30 mixture of SO2 and SO3, in dry or moist conditions and at low and high temperature, and were evaluated before and after regeneration at 550 °C. After SOx exposure, a high degree of deactivation is observed at temperatures below 300 °C. A major part of this deactivation is reversible by heating to 550 °C for 4 h, while a smaller, but appreciable, level of irreversible deactivation remains.

The presence of water always increases irreversible deactivation, but has no apparent effect on reversible deactivation. Exposure to SOx at 200 °C, always leads to a higher level of irreversible deactivation compared to exposure at 550 °C. The presence of SOx at 200 °C leads to significantly stronger deactivation; at 550 °C, deactivation by SOx is not significantly different from that by SO2. Regeneration of Cu-CHA exposed to SO2 at 200 °C is accompanied by a decomposition of SOx and release of SO2 around 400 °C.

In all experiments, the reversible deactivation accounts for most of the total deactivation, which makes regeneration by heating to 550 °C, an easily obtainable temperature in exhaust systems, a realistic approach to deal with deactivation by SOx.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apcatb.2017.12.018.

References

Chapter 3
Chapter 4

STEM-EDX investigation of the S distribution in the zeolite crystals of an SO$_2$ exposed Cu-CHA catalyst
Introduction

In the previous section of this chapter, the cause of the reduction of the apparent activation energies in the SO$_2$ exposed catalyst, to about half the value for the fresh catalyst was discussed. Such a decrease to the apparent activation energy can be the result of diffusion limitation. The possibility of introducing diffusion limitations to the SCR reaction by the presence of sulfur was assessed by evaluation of the efficiency factor of the catalyst. In order to get into a diffusion limited regime where the activation energy is affected, the diffusion coefficient had to be lowered by a factor 100. Assuming that sulfur was evenly distributed in the Cu-CHA crystals at the Cu sites, it was argued that the sulfur content corresponding to about 20% coverage of the Cu content could not infer such dramatic changes to the diffusion coefficient. However, if the sulfur is located in the outer shell of the zeolite crystals, it may have a larger impact on the diffusion of the reactants into the zeolite. Therefore, the distribution of sulfur in the Cu-CHA crystals is investigated by scanning transmission electron microscopy with energy dispersive X-ray (STEM-EDX) spectroscopy.

Experimental

For the STEM-EDX measurements, a fresh Cu-CHA catalyst (Si/Al = 14.6 and Cu/Al = 0.42) was exposed to SO$_2$ at 200 °C for 1 h, resulting in a S/Cu ratio of 0.28, as determined by ICP. The same catalyst was used in Chapter 5, where the SO$_2$ exposure is described in more detail.

STEM-HAADF (high-angle annular dark-field imagining) images and STEM-EDX measurements were made in a FEI Talos 200FX electron microscope. The fresh Cu-CHA catalyst was mounted on a gold grid, while the SO$_2$ exposed Cu-CHA catalyst powder was mounted on a Cu grid due to some overlap in the electromagnetic spectrum of gold and sulfur.

Results and discussion

The images of the fresh and SO$_2$ exposed Cu-CHA catalysts, and distributions of Cu and S from the EDX measurements are shown in Figure 1.
Figure 1 – Top left) STEM-HAADF image of fresh Cu-CHA catalyst, Top right) Cu distribution in fresh Cu-CHA from STEM-EDX, Middle left) STEM-HAADF image of SO$_2$ exposed Cu-CHA, Middle right) S distribution in SO$_2$ exposed Cu-CHA from STEM-EDX, Bottom left) S and Si distribution in SO$_2$ exposed Cu-CHA from STEM-EDX and indication of linescan area, Bottom right) relative concentrations of Cu (green), Al (red), Si (blue) and S (yellow) from the linescan. The relative concentration of S has been scaled, which is the reason for the higher noise level for that element.
In the fresh Cu-CHA catalyst, Cu appears evenly distributed in the crystal with small areas of Cu clustering. Similarly, the S appears to be evenly distributed in the entire zeolite crystal. This is also confirmed by the relative concentrations of S, Si, and Al obtained in the linescan. This indicates that the change in the activation energies of the SO$_2$ exposed catalysts is not a result of sulfur accumulation in the outer shell of the Cu-CHA zeolite crystals.

With STEM-EDX the Al/S ratio is measured to be 8 in the SO$_2$ exposed catalyst, and with a Cu/Al ratio of 0.42, it corresponds to a S/Cu ratio of about 0.3, which is close to the S/Cu ratio of 0.28 measured with ICP. This adds to the verification of the STEM-EDX measurements.

**Conclusions**

The sulfur distribution in an SO$_2$ exposed Cu-CHA catalyst was measured with STEM-EDX, which showed that sulfur was evenly distributed in the Cu-CHA zeolite crystal. This supports the conclusion in Chapter 3 that the change in the activation energy after SO$_2$ exposure is not a result of diffusion limitations.
Chapter 5

Impact of SO$_2$-poisoning over the lifetime of a Cu-CHA catalyst for NH$_3$-SCR

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Impact of SO2-poisoning over the lifetime of a Cu-CHA catalyst for NH3-SCR

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ABSTRACT

Cu-CHA catalysts for NH3-SCR in exhaust after treatment systems of heavy-duty vehicles, are constantly exposed to SO2 during their lifetime of about 10,000 h. In order to study the development of deactivation by SO2, a Cu-CHA catalyst was exposed to SO2 at 200, 300, 400 and 500 °C for different durations up to 120 h, resulting in total SO2 exposures that are comparable to that of the lifetime of a Cu-CHA catalyst in an after treatment system. The measured deactivation increases very fast to a steady level in the range 0.85–0.95, dependent on the exposure temperature, which shows the need for frequent regeneration of the catalyst. Regeneration at 550 °C can restore the activity of the catalyst to 80% of its fresh activity level even after 120 h exposure, suggesting frequent regeneration as a feasible method for overcoming SO2-poisoning. ICP analyses showed that SO2 exposure led to S/Cu ratios in the range 0.5–1, indicating that sulfur is associated with Cu. After regeneration the S/Cu ratios did not exceed 0.2, suggesting that only certain Cu sites are able to form Cu,S species that are thermally stable above 550 °C. This together with the observations that the deactivation before and after regeneration impact differently on the activation energy of the SCR reaction, and that the deactivation never exceeded 0.95, suggests that SO2-poisoning of Cu-CHA depends on the structural properties of this material. TGA measurements of the mass uptake during SO2 exposure was consistent with a process where SO2 is initially adsorbed on Cu, and then slowly oxidized to SO3 at 200 °C, whereas the mass uptake at 500 °C was consistent with an immediate adsorption of SO2, which is accredited to a faster oxidation rate at higher temperature.

1. Introduction

Combustion engines in vehicles produce polluting compounds, and their emissions are restricted by legislation. In particular, the emissions of NOx (NO and NO2) from vehicles is strictly regulated, which already has resulted in a significant improvement of air quality [1]. For diesel engines, the most effective method to reduce NOx emissions to the level required by legislative regulations, is by selective catalytic reduction (SCR). Current aftertreatment systems contain one or more catalytic converters for NH3-SCR [2]. A widely used technique for dosing of NH3 in exhaust aftertreatment systems is by injection of aqueous urea, which decomposes to NH3 above 180 °C [2], setting a lower temperature limit for NH3-SCR in an exhaust system. Furthermore, the improved fuel efficiency of diesel engines that has been achieved in recent years, in order to lower the CO2 emissions, has resulted in colder exhaust gas. Consequently, it takes longer time to heat the catalysts in the exhaust aftertreatment system, and therefore, the low-temperature activity, in particular around 180 °C, has become more important for the abatement of NOx emissions.

Currently employed SCR catalysts are V2O5-based or zeolites containing Fe or Cu. Especially Cu-zeolites of the CHA topology are very active in the low-temperature range 180–300 °C, which in combination with their high hydrothermal stability and low N2O selectivity, has made these materials particularly interesting as SCR catalysts for automotive applications [2–4]. The Al centers in the zeolite framework generates locations with negative charge, which are balanced by external cations. In the case of Cu-CHA, Cu in these ion-exchange positions gives rise to the activity of the Cu-CHA catalysts for the NH3-SCR reaction. Cu-CHA catalysts have two characteristic activity regimes, namely a low-temperature (approx. 200–300 °C) and a high-temperature (> 350 °C) [5], which are separated by a region where the steady state NOx conversion actually can decrease with increasing temperature [6]. The low-temperature activity of Cu-CHA catalysts is ascribed to the formation of mobile [Cu(NH3)2]+ complexes in the presence of NO and NH3, which enables formation of Cu pairs that efficiently dissociate O2 [7–14], which is a key step in the NH3-SCR reaction.

A drawback of Cu-zeolite catalysts is their sensitivity to SO2. SO2 is formed by oxidation of sulfur-containing compounds in the fuel and engine lubrication oils. In practice, the formation of SO2 is limited by...
reduction of the sulfur content in diesel fuels, and therefore, the use of ultra-low sulfur diesel (ULSD) has been implemented in USA and Europe. The current maximum allowable sulfur concentration in ULSD is 15 wt ppm in USA and 10 wt ppm in Europe [1]. The use of ULSD results in a typical SO2 concentration in the exhaust gas in the range 0.5–2 volume ppm SO2. Even at such low SO2 concentrations, a considerable deactivation of Cu-CHA catalysts, particularly in the low-temperature regime, is still observed [6,15–22].

The differences in the effect of SO2 on the performance of the different types of NH3-SCR catalysts is clearly related to the chemistry of the system [2,3]. The high SO2 sensitivity for Cu-zeolites, compared to Fe-zeolites, is possibly due to the higher stability of Cu-sulfate compared to Fe-sulfate [23]. This is consistent with the observed release of SO2 and restoration of activity of Cu-CHA by heating to 700 °C, which is above the temperature for thermal decomposition of Cu-sulfate [6,18,22,23]. This suggests that the deactivation induced by SO2 is at least partially due to the formation of some SO3. In an aftertreatment system, SO2 can form from oxidation of SO2, which can take place over the diesel oxidation catalyst and also in the Cu-CHA catalyst itself [6,15,18,20]. Therefore, to understand the deactivation of Cu-zeolite catalysts by SO2, the formation and interaction of SO3 with Cu must be considered as well. This means that the SO2-induced deactivation of Cu-zeolites is influenced by many factors, such as temperature, gas environment, and oxidation of SO2 to SO3 [6,15,18,22], and several Cu,S species of varying stability that can be formed [6,15–18,22,24,25]. A potentially feasible method for treating SO2-induced deactivation of Cu-CHA catalysts in an exhaust system is by thermal regeneration of the catalyst, which is possible due to the different stabilities of the Cu,S species [6,15,18,20,22,26]. In a typical modern aftertreatment system, an achievable maximum temperature of the SCR catalyst for regeneration is about 550 °C. Regeneration of a Cu-CHA catalyst at this temperature reverses the predominant part of the deactivation [6]. Thus, the total deactivation measured after exposure to SO2 can be divided into a reversible and an irreversible part, by measuring the irreversible deactivation after regeneration at 550 °C [6].

The required lifetime of an SCR catalyst in an aftertreatment system of a heavy-duty diesel vehicle is about 10,000 h. Throughout its lifetime, the SCR catalyst is constantly exposed to low concentrations of SO2, which makes the deactivation a continuous process persisting over the lifetime of the catalyst. Therefore, it is important to know the impact of these low SO2 concentrations over long-term SO2 exposure. The deactivation process can be accelerated by increasing the SO2 concentration [22], because the deactivation appears to depend on the total SO2 exposure [22], defined as the product of the SO2 concentration and the exposure time. In this way, the development of the reversible and irreversible deactivation over the lifetime of the catalyst can be assessed from experiments of significantly shorter exposure times, but with higher SO2 concentrations.

In this contribution, the deactivation and regeneration of a Cu-CHA catalyst is investigated for SO2 exposures of increasing duration up to 120 h and with 50 ppmv SO2, which is comparable to the total SO2 exposure of a commercial Cu-CHA SCR catalyst during its required lifetime. The deactivation is evaluated by comparing the performance of the catalysts in the NH3-SCR reaction after SO2 exposure at 200–500 °C, and after regeneration at 550 °C, to that of the fresh. This is important, in order to assess the impact of the reversible and irreversible deactivation development over long-term SO2 exposure. Furthermore, the catalytic performance is compared to the S uptake of the catalysts exposed at 200–500 °C, as determined by ICP, and to in situ thermogravimetric measurements of SO2 exposure at 200 and 500 °C.

2. Experimental

The zeolite material used in this study is a CHA zeolite with a Si/Al ratio of 14.6. Cu was introduced in the zeolite by mixing it with the appropriate amount of an aqueous Cu(NO3)2 solution to obtain 2.5 wt% Cu in the zeolite. After mixing, the slurry was dried at 120 °C and calcined at 550 °C for 3 h. The calcined catalyst powder was light blue, indicating that Cu is located in the ion-exchange positions of the CHA material. The Si, Al and Cu content were determined by ICP-OES to be 37.5, 2.46, and 2.43 wt%, respectively, corresponding to a Cu/Al ratio of 0.42, and estimated 2.76 wt% Cu on a dry matter basis.

The SO2 exposures were carried out in a flow reactor setup, equipped with 4 parallel quartz reactor tubes, each with independent control of the temperature. A sample of 1.6 g of fresh catalyst powder (sieve fraction 150–300 μm) was loaded in each reactor tube and held in place by quartz wool plugs. Prior to SO2 exposure, all catalyst loadings were heated to 500 °C for 2 h in a flow of 10% O2, 5% H2O, and sufficient N2 to obtain a total flow rate of 1.67 N L/min. Then, one reactor was kept at 500 °C, and the other three reactors were cooled to 200, 300, and 400 °C. For the SO2 exposure, 50 ppmv SO2 was added to the reactor feed, while keeping the same total flow rate. In 6 different runs, the duration of SO2 exposure was varied and chosen as 1, 5, 15, 30, 65, 120 h. In this way, a total of 24 catalyst samples were obtained, each with different SO2 exposure duration and temperature. Finally, 0.8 g of each of these 24 samples was regenerated in the same parallel reactor setup by exposing to 550 °C for 6 h in a flow of 10% O2, 5% H2O, and N2 to balance the flow to 1.67 N L/min.

This yields a total of 48 treated catalyst samples, 24 exposed to SO2 and 24 regenerated, which were all analyzed for Cu and S content using ICP-OES in order to determine the S/Cu ratio after each treatment of the catalyst.

The NH3-SCR activity measurements were done in a microreactor setup, by adding 5 mg (dry matter basis) catalyst powder, 150–300 μm sieve fraction, to a quartz U-tube reactor with an inner diameter of 2 mm, using quartz wool to keep the catalyst in place. The reactor feed gas consisted of 500 ppmv NO, 533 ppmv NH3, 10% O2, 5% H2O, in N2 at a total flow rate of 225 N mL/min. To measure the NH3-SCR activity, the catalyst was heated prior to 160, 190, 200, 210, 220, 250, 300, 325, 350, 400, and 550 °C and kept at these temperatures for 40 min to ensure stationary conditions. The concentrations of NO, NH3, NOx, and N2O in the reactor exit gas were monitored continuously by a Gasmet CX4000 FTIR analyzer, connected to the reactor outlet. The feed gas concentrations were measured by bypassing the reactor, using the same FTIR analyzer.

To determine the NH3-SR activity, the steady state conversion was determined from the activity measurement, and converted to a rate constant according to:

\[ k = \frac{F}{W \ln(1-X)} \]  

where \( F \) is the total molar flow rate, \( W \) is the catalyst mass, and \( X \) is the NO conversion. For the deactivation we use our earlier definition [6] in which the rate constants of the catalysts exposed to SO2 before or after regeneration \( k \) are related to the corresponding rate constant of the fresh catalyst \( k_{\text{fresh}} \), as expressed in:

\[ \text{Deactivation} = 1 - \frac{k}{k_{\text{fresh}}} \]  

Finally, the uptake of sulfur at 200 °C and 500 °C was followed by thermogravimetric analysis (TGA) in two separate measurements. For these measurements, a sample of the fresh catalyst was heated to 550 °C for 1 h in 10% O2 in N2 at a total flow rate of 150 N mL/min, to obtain the dry mass of the catalyst. The dry masses of the samples used were 25.9252 mg (S uptake at 200 °C) and 37.6135 mg (S uptake at 500 °C). Then, the catalyst was exposed to SO2 at 200 °C or 500 °C, using a feed gas consisting of 50 ppmv SO2, 3% H2O and 10% O2 in N2, also at a total flow rate of 150 N mL/min, while monitoring the change in catalyst mass. Changes in catalyst mass during regeneration were obtained by heating to 550 °C and changing the feed gas to 10% O2 in N2, while keeping the same total flow rate. The changes in S uptake are...
determined from the weight changes in alternating SO2 exposure and regeneration phases at a fixed temperature (200 or 500 °C), where catalysts are regenerated after the same cumulative durations of the SO2 exposure as used in the deactivation measurements given above.

3. Results

Fig. 1 shows the development of the steady state NO conversions as function of the temperature over the duration of exposure to SO2 at 200 °C, and after subsequent regeneration by heating at 550 °C for 6 h. In all cases, the NO conversion in the temperature range 160-350 °C is considerably lower after exposure to SO2, compared to the fresh catalyst. Regeneration at 550 °C mostly restores the NO conversion in that temperature range. The same trends are observed after exposure to SO2 at 300 °C, 400 °C, and 500 °C, see supporting information. This behavior can be described in terms of reversible and irreversible deactivation as defined earlier [6]. The deactivation remaining after regeneration is then the irreversible deactivation, and the reversible deactivation is defined as the difference in deactivation of the SO2 exposed catalyst before and after regeneration [6].

The total SO2 exposure, which corresponds to the product of the exposure time and SO2 concentration, appears to be a good descriptor for deactivation by SO2 [22], which also allows for estimation of the deactivation over the entire required lifetime of the catalyst. Fig. 2 summarizes the development of the reversible and irreversible deactivation with SO2 exposure for the exposure temperatures of 200, 300, 400, and 500 °C, along with the corresponding S/Cu ratio measured by ICP. Both the reversible and irreversible deactivation initially show a fast increase with SO2 exposure, and reach a final level after an SO2 exposure of 500–1000 ppm h, after which the deactivation remains constant. It is noted that the predominant part of the final deactivation level is reached already after 50 ppm h, which is the first data point in each SO2 exposure series, indicating that the effect of SO2 is almost immediate. The final deactivation after SO2 exposure, before regeneration, is 0.85–0.95 and depends on the temperature of SO2 exposure. The irreversible deactivation is about 0.2–0.3, independent of the temperature for SO2 exposure. It is also noted that we have not found any conditions in which a complete deactivation of the Cu-CHA is observed.

In order to relate the measured deactivation of the Cu-CHA catalyst with the sulfur uptake, the deactivation is compared to the measured S/Cu ratios before and after regeneration. The S/Cu ratios of the regenerated states of the catalyst mirrors the observed irreversible deactivation, with a rapid increase during the first 1000 ppm h SO2, followed by a constant final level of about 0.2, independent of the temperature of SO2 exposure. This value matches the observed deactivation level of 0.2–0.3 quite well, suggesting that the irreversible deactivation is related to the adsorption of sulfur on the active Cu sites.

The measured S/Cu ratios before regeneration do not appear to reach a final level. The S/Cu ratios initially increase fast, which parallels the fast increase of the deactivation, but after about 1000 ppm h SO2, the S/Cu ratio continues to increase at a lower rate, except for the catalysts exposed to SO2 at 500 °C. The measured S/Cu ratios are, in most cases, lower than the observed level of deactivation, which indicates that the reversible deactivation cannot be directly explained by Cu site blockage with sulfur. Nevertheless, the observation that the S/Cu ratios generally are lower than 1 indicates that the uptake of sulfur is related to the Cu and is consistent with adsorption of sulfur on Cu.

A more detailed comparison of the measured S/Cu ratios and the reversible and irreversible deactivation is shown in Fig. 2B. The irreversible deactivation is always disproportionately larger than the corresponding S/Cu ratios, while the irreversible deactivation generally is closer to a 1:1 correlation with the S/Cu ratio, which would be expected for deactivation by single site blocking. This shows that the impact of sulfur uptake on the reversible deactivation is larger compared to the irreversible deactivation. This also suggests that the reversible and irreversible deactivation are related to the formation of different Cu,S species or selective adsorption of sulfur on specific Cu sites.

The difference between reversible and irreversible deactivation is also reflected in the apparent activation energy for the NH3-SCR reaction. Fig. 4 shows the apparent activation energies for the different SO2 exposures before and after regeneration. Clearly, for the catalysts before regeneration, the activation energy is lowered from about 70 kJ/mol to about 30 kJ/mol for an SO2 exposure of about 1000 ppm h, which coincides with the observed fast increase in deactivation and initial uptake of sulfur. At longer SO2 exposures, the apparent activation energy remains constant. For the regenerated catalysts, all measured activation energies are about 70 kJ/mol, which is close to the value of the fresh catalyst, independent of SO2 exposure time or temperature. This means that the level of deactivation of the Cu-CHA catalyst by SO2 is not only the result of a certain amount of S in the catalyst, but also depends on which Cu,S species that are present. The different trends observed for the activation energies before and after regeneration are also relected in the diagram of different mechanisms for the SCR reaction on the reversibly and irreversibly deactivated Cu-CHA catalysts, in agreement with an earlier conclusion [6].

The different influence of the SO2 exposure temperature on the sulfur uptake related to the reversible or irreversible deactivation is illustrated in Fig. 5, which shows the measured S/Cu ratios as function of the exposure temperatures. As also noted above, the S/Cu ratios related to the irreversible deactivation reach approximately 0.2 for all exposure temperatures, which suggests that the irreversible deactivation is related to the formation of a Cu,S species at certain Cu sites. The S/Cu ratios related to the reversible deactivation in Fig. 5 show a maximum sulfur uptake at 400 °C for short SO2 exposure (1 and 5h), and at 300 °C for the longer SO2 exposures. This trend is similar to that observed on a Cu/SAPO-34 catalyst exposed to SO2 in O2 and H2O at different temperatures [22], and reflects a trade-off between the kinctics of the formation of the Cu sulfite species and the equilibrium adsorption concentration [22].

TGA measurements were used to assess the sulfur uptake during SO2 exposure at 200 °C and 500 °C in more detail, to better understand the effect of SO2 at low and high temperature. Fig. 6 shows how the relative mass of the catalyst (with the dry mass of the catalyst before SO2 exposure as basis) changes with the total SO2 exposure. Both at 200 °C and 500 °C, SO2 exposure leads to a steep increase in the catalyst mass at SO2 exposures below 500 ppm h. At 500 °C, a relative mass of 1.02 is reached, which remains stable after longer exposures to SO2, while at 200 °C, the relative mass initially increases to 1.01, which then increases further to approximately 1.03 after 6000 ppm h SO2 exposure. This is qualitatively the same trend as found for the S/Cu ratio (Fig. 2), which is an indication that the observed increase in catalyst mass is indeed due to the uptake of SO2.

For a more precise interpretation of the observed increase in catalyst mass upon exposure to SO2 at 200 °C and 500 °C, we need to know in
which form the SO3 is adsorbed on the catalyst. The most obvious options are adsorption of SO2 or SO3, and the formation of sulfites and sulfates on the Cu sites [6,15,16,18,22]. By comparing the observed increases in catalyst mass measured in the TGA experiments with the measured S/Cu ratios given in Figs. 2 and 5, it is possible to work out whether the sulfur is adsorbed as SO2 or SO3. First, the observed increase in catalyst mass is converted to a molar amount of sulfur, under the assumption that the sulfur is present as either SO2 or SO3, which together with the known Cu content, 2.76 wt% on dry matter basis, results in an estimated SO2/Cu and SO3/Cu ratio. In Fig. 7, these
estimated SO$_2$/Cu and SO$_3$/Cu ratios are compared to the measured S/Cu ratios determined by ICP, for Cu-CHA exposed to SO$_2$ at 200 °C and 500 °C. At an SO$_2$ exposure temperature of 200 °C, the SO$_2$/Cu ratios follow the measured S/Cu ratios to 1000 ppm h of SO$_2$ exposure. At 6000 ppm h SO$_2$, the measured S/Cu ratio matches the estimated SO$_2$/Cu ratio. This indicates that initially it is SO$_2$ that is adsorbed on the Cu, but it is slowly oxidized to SO$_3$. With an SO$_2$ exposure temperature of 500 °C, the estimated SO$_2$/Cu ratio matches the S/Cu ratio over the entire SO$_2$ exposure duration. This clearly shows that at 500 °C, oxidation of SO$_2$ is faster, and adsorption is essentially as SO$_3$. Adsorption of SO$_3$ on a Cu-OH species actually corresponds to the formation of a bisulfate species, which have been proposed earlier as being the cause of the irreversible deactivation [6,15,16,18–22,24,25].

4. Discussion

The results presented above clearly show that SO$_2$ primarily affects the low-temperature activity of Cu-CHA catalysts for SCR, and therefore, the impacts of SO$_3$ on the high-temperature activity will not be discussed further here.

For an SCR catalyst that has a required lifetime of about 10,000 h, it is important to be able to estimate the performance for the entire lifetime. One way to do this is by comparison of the total SO$_2$/Cu exposure for the lifetime of the catalyst in a heavy-duty vehicle to similar conditions in a test. The total SO$_2$/Cu exposure for a Cu-CHA catalyst over its lifetime is about 44, assuming that the vehicle covers 800,000 km with a consumption of 30 L/100 km, using 5 wt ppm S diesel, and with a Cu-loading of 45 g of the Cu-CHA SCR catalyst. The total molar SO$_2$/Cu exposure in the experiments presented in this article is 41.7 after 120 h, which is similar to the typical SO$_2$/Cu exposure in an exhaust system. Therefore, we expect that the development of SO$_3$-poisoning in our experiments reflect that of a Cu-CHA SCR catalyst in an exhaust after-treatment system.

The results presented in this study shows that the reversible deactivation increases fast to a high level, independent of the SO$_2$ exposure temperature. This means that the SCR catalyst in an exhaust system requires frequent regeneration in order to maintain an efficient NH$_3$-SCR performance, especially in the context of cold start where the low-temperature activity is particularly important. Based on the presented results, it is actually possible to restore the predominant part of the original activity of the catalyst throughout its lifetime, by regeneration at 550 °C. This shows that SO$_2$-poisoning of Cu-CHA catalysts is occurring over the lifetime of the catalyst, but that it can be managed by proper regeneration strategies. Furthermore, the irreversible deactivation seems sufficiently small to be handled by appropriate system design.

The use of Cu-CHA catalysts in exhaust systems appears to rely on the efficiency of regeneration, which likely depends on the SO$_2$ concentration during regeneration. Thus, exposure to 50 ppmv SO$_2$ at 500 °C leads to uptake of sulfur by the catalyst, while regeneration at 550 °C in the absence of SO$_2$ partially removes sulfur from the catalyst. Furthermore, reversible and irreversible deactivation of a Cu-SAPO-34 catalyst have been shown to build up when exposed to SO$_2$ concentrations as low as 1.5 ppmv at 500 °C [22]. Therefore, it appears that the uptake or removal of sulfur depends on the SO$_2$ concentration being above or below a critical value, which is somewhere in the range 0–1.5 ppmv SO$_2$. This could potentially complicate the regeneration if the SO$_2$ content of the exhaust gas is above the critical concentration, in which case a regeneration would resemble the SO$_2$ exposure at 500 °C. In that case, the low-temperature activity of Cu-CHA catalysts would be lost relatively fast, and so would the main advantage of using these materials compared to Fe-zeolites or vanadia-based systems. The efficiency of regeneration, and the critical SO$_2$ concentration, would have to be verified in an actual exhaust system, since reducing compounds in the exhaust gas, such as hydrocarbons and NH$_3$, have been shown to have a beneficial effect for removing sulfurous compounds from Cu-CHA catalysts [26].

The process for the uptake of sulfur by the Cu-CHA catalyst possibly proceeds by an initial adsorption of SO$_3$ on Cu where the sulfur is subsequently oxidized to sulfate. This is envisioned because the Cu-CHA...
catalyst is exposed to SO₂, which must oxidize in order to constitute the forms of sulfate that are associated with the Cu₅ species causing the reversible [6,15,16,18,22] and irreversible deactivation [6,22]. The proposed process is consistent with the results from the TGA experiment at 200 °C (Fig. 7), where the initial mass uptake fits with an uptake of SO₃, and over time changes to fit better with an uptake of SO₂. At this temperature (200 °C), there is a clear difference between the initial and final uptake, which indicates that the oxidation of SO₂ is kinetically controlled. In the TGA experiment at 500 °C, the mass uptake fits with a constant uptake of SO₂, which can be explained by a faster oxidation of SO₂ at this temperature [20,22], which both could be on the Cu sites or in the gas phase.

A possible reason for the disproportionally high reversible deactivation, as compared to the S/Cu ratio, is that the adsorption of SO₂ affects the mobility and effective amount of [Cu(NH₃)₂]⁺ ions in the Cu-CHA zeolite. The current understanding of the low-temperature part of the SCR mechanism is that the mobile [Cu(NH₃)₂]⁺ complexes allow for the formation of pairs of Cu ions, which are crucial for the dissociation of the oxygen molecules [8,11]. As a consequence, the activity depends on the amount of Cu below a certain Cu loading, and depends linearly on the Cu density above it [8]. This results in two distinct activity regimes, which may be related to the different impacts of the sulfur loading on the reversible and irreversible deactivation. In principle, the mechanism based on mobile [Cu(NH₃)₂]⁺ complexes implies that all Cu sites are the same, namely the mobile [Cu(NH₃)₂]⁺ complex, and contribute equally to the activity. Ultimately, the activity is determined by the amount of Cu pairs that are formed at the given conditions. The different trends for the activation energy of the SCR reaction with reversible and irreversible deactivation, as shown in Fig. 4, and the disproportionately larger reversible deactivation than irreversible deactivation as compared to the S/Cu ratios shown in Fig. 3 can be understood in relation to the two activity regimes. Since the S/Cu ratios related to the irreversible deactivation are always lower than those related to the reversible deactivation, and lower than 0.2, the amount of deactivated Cu in these cases may be sufficiently small to keep the amount of non-deactivated Cu in the linear dependence regime. The activity is thus not limited by formation of Cu pairs, and the deactivation would simply correspond to a loss of active sites, which is also consistent with the values of the activation energies close to that of the fresh catalyst. For the reversible deactivation, the S/Cu ratios of 0.3–1 could enforce a situation where the effective Cu content becomes sufficiently low for the activity to be restricted by formation of Cu pairs. In this situation, the activity depends on the amount of effective Cu density, and therefore, it would be expected that the deactivation is disproportionately larger than the S/Cu ratio, as observed in Fig. 3. The lower activation energy is then related to the fact that the rate of the SCR reaction is determined by the limited rate of Cu pair formation.

The observation that similar sulfur contents can result in significantly different levels of reversible and irreversible deactivation [6] is not consistent with the idea that all Cu sites contribute equally to the rate of the NH₃-SCR reaction. Factors like the zeolite structure and Al distribution can also influence the reactivity or mobility of Cu, eventually resulting in Cu sites of different activity. This idea is supported by two observations of the SO₂ exposed and regenerated Cu-CHA catalyst in Fig. 2. The first observation is that the reversible deactivation never exceeds 0.95, indicating that some Cu does not adsorb SO₂ or is not affected by SO₂, and the second observation is that the S/Cu ratio related to the irreversible deactivation is limited to 0.2, suggesting that the more stable Cu sulfate species can only form at certain Cu sites. According to this view, the deactivation and regeneration behavior of Cu-CHA catalysts also depend on the structural properties of the catalyst.

5. Conclusion

A Cu-CHA catalyst for NH₃-SCR has been exposed to SO₂ at different temperatures in the range 200–500 °C, and at durations up to 120 h, resulting in a total SO₂ exposure that is similar to what an SCR catalyst experiences over the entire lifetime in an exhaust aftertreatment system on a heavy-duty vehicle. Activity measurements after SO₂ exposure, and after regeneration at 550 °C, enabled measurement of the extent of deactivation of the catalyst in these two states. The deactivation of the low-temperature activity of the Cu-CHA catalyst in the presence of SO₂ occurs fast in the entire temperature window 200–500 °C to a final deactivation level in the range 0.85–0.95, dependent on the exposure temperature. Heating in SO₂-free gas to 550 °C restores the activity to about 80% of its original level, even after a total S/Cu exposure similar to that of the lifetime of a Cu-CHA SCR catalyst in a heavy-duty diesel aftertreatment system. This suggests regeneration as a feasible method for handling SO₂-poisoning, since proper dimensioning of the catalyst easily can treat the irreversible deactivation of maximum 0.2–0.3 that develops over long-term SO₂ exposure. Analogous to the deactivation, the S/Cu ratios also increase fast initially, and the S/Cu ratios of the SO₂ exposed catalysts reach different levels in the range of 0.5–1, dependent on the exposure temperature. The regenerated S/Cu ratios never exceed 0.2, indicating that the irreversible Cu₅ species are restricted to certain Cu sites. The mechanism of the sulfur uptake appears to proceed by an initial uptake of SO₂ by the catalyst, followed by oxidation to sulfate on the catalyst, at a rate that increases with temperature.
Chapter 5

The reversible and irreversible deactivation have a different impact on the low-temperature SCR mechanism, which is seen by i) a disproportionately larger reversible deactivation relative to the S/Cu ratio as compared with the irreversible deactivation, and ii) by the reversible deactivation causing a change in the activation energy of the SCR reaction, whereas the irreversible deactivation does not. This, together with the observations of a maximum irreversible S/Cu ratio of 0.2, and a maximum deactivation level of 0.95, points to a dependence of the SO2-poisoning of Cu-CHA catalysts on structural properties of the Cu-CHA material.

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Declarations of interest

None.

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References

Chapter 6

Site selective adsorption and relocation of \( \text{SO}_x \) in deactivation of Cu-CHA catalysts for \( \text{NH}_3 \)-SCR

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Site selective adsorption and relocation of SO\textsubscript{x} in deactivation of Cu-CHA catalysts for NH\textsubscript{3}-SCR

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Abstract

The presence of SO\textsubscript{2} in diesel exhaust gases causes severe deactivation of the Cu-CHA catalysts for the reduction of NO\textsubscript{x} by selective catalytic reduction with ammonia (NH\textsubscript{3}-SCR). The deactivation of Cu-CHA catalysts after exposure to SO\textsubscript{2} at 550 °C for 0.5, 4, 8, 16 and 32 h, and subsequent regeneration in SO\textsubscript{2}-free gas at 550 °C was related to the site-dependent interactions of SO\textsubscript{2} with Cu ions associated with one or two framework Al centers (Z-CuOH or Z\textsubscript{2}-Cu), as determined by electron paramagnetic resonance (EPR). SO\textsubscript{2} primarily interacts with the EPR-silent Z-CuOH sites, but a new, EPR-active Z\textsubscript{2}-Cu phase develops with SO\textsubscript{2} exposure time as well. A part of the original Z\textsubscript{2}-Cu species remain unaffected by SO\textsubscript{2}, which is associated with a maximum deactivation level of about 90%. Regeneration at 550 °C leads to the release of most of the SO\textsubscript{2} from the Z-CuOH sites and some relocation of sulfur to Z\textsubscript{2}-Cu sites occurs. The activation energy for NH\textsubscript{3}-SCR on the SO\textsubscript{2} exposed catalysts decreases with S content from about 65 kJ/mol to 30 kJ/mol. For the regenerated catalysts, the activation energy is restored to about 65 kJ/mol, showing the importance of the Z-CuOH sites for the NH\textsubscript{3}-SCR reaction.

Introduction

The selective catalytic reduction of NO\textsubscript{x} (NO and NO\textsubscript{2}) with NH\textsubscript{3} (NH\textsubscript{3}-SCR) is the predominant method for removal of NO\textsubscript{x} from exhaust gas of heavy-duty diesel vehicles. The catalysts used for this reaction are based on V\textsubscript{2}O\textsubscript{5}, Fe-zeolites or Cu-zeolites. Future legislation will require tighter NO\textsubscript{x} emission limits, and therefore, a more efficient removal of NO\textsubscript{x} in the low-temperature region becomes crucial. In this respect, the Cu-zeolites with the CHA structure are attractive\textsuperscript{1,2} because of the significantly higher activity of the Cu-CHA catalysts at low temperatures down to 180 °C, which is unmatched by Fe-zeolites and V\textsubscript{2}O\textsubscript{5}-based catalysts\textsuperscript{1,3,4}.
According to the current understanding, the low-temperature activity of Cu-CHA catalysts is related to the ability to form mobile \([\text{Cu(NH}_3\text{)}_2]^+\) complexes. These complexes facilitate the formation of Cu pairs\(^5,6\) on which the dissociation of oxygen can take place\(^5-12\).

A drawback of Cu-CHA catalysts, and Cu-zeolite based catalysts in general, is their sensitivity to SO\(_2\) in the exhaust gas that originates from the sulfur present in the fuel. Ultra-low sulfur diesel contains less than 10 wt ppm (Europe) or 15 wt ppm (US) sulfur, and the SO\(_2\) concentration in the exhaust gas typically reaches a few ppmv, which is nevertheless sufficient to reduce the low-temperature activity of the Cu-CHA catalysts significantly\(^13,14,23,24,15-22\). To be able to preserve the good low-temperature activity, it is important to understand the impact of SO\(_2\) on the NH\(_3\)-SCR activity of Cu-CHA based catalysts.

We have recently shown that deactivation of Cu-CHA catalysts depends on the total SO\(_2\) exposure, which is the product of the SO\(_2\) concentration and the exposure time\(^14\). Deactivation by SO\(_2\) is almost immediate: at about 1% of the total lifetime exposure to SO\(_2\), the activity is reduced to about 30% of the original activity, and it stabilizes at about 10% of the original activity after 5-10% of the lifetime SO\(_2\) exposure\(^15\). The sulfur uptake in the Cu-CHA catalyst follows a similar pattern as the activity and, dependent on the temperature, a maximum S/Cu molar ratio of 0.5-1 is reached. The observation that the S/Cu ratio usually does not exceed 1 points to the formation of Cu,S species\(^13-15\). Thermal regeneration at 550 °C, which is feasible in a typical EURO VI exhaust system, can restore most of the activity if carried out in SO\(_2\)-free gas\(^13-15\). During the regeneration, SO\(_2\) is released from the catalyst, but a certain fraction of the sulfur is retained in a stable form that resemble Cu sulfate\(^13-17,20\). The observations that heating to 550 °C results both in a partial regeneration of Cu-CHA catalysts and in the formation of a certain amount Cu sulfate, indicates that there are distinct Cu sites with a different reactivity towards SO\(_2\)\(^13,15,20,23\).

The most obvious possibility for distinct Cu sites in Cu-CHA catalysts is that the Cu can be associated with either one or two Al centers in the zeolite framework. This leads to two main Cu\(^{II}\) sites: Z-CuOH and Z\(_2\)-Cu, and these sites have different chemical properties\(^10,25-30\). The relative amounts of these Cu sites depend on synthesis conditions, the Si/Al ratio of the zeolite, and the Cu loading\(^10\). Therefore, it is important to understand which role the Z-CuOH sites and Z\(_2\)-Cu sites play in the deactivation by SO\(_2\).

Electron paramagnetic resonance (EPR) spectroscopy is a powerful method for selective monitoring of the Z\(_2\)-Cu sites in Cu-CHA catalysts, and the presence of sulfur-species on these sites can be detected. In this article, EPR is used in combination with elemental analysis to localize sulfur in SO\(_2\) exposed and regenerated Cu-CHA catalysts after total SO\(_2\) exposures up to 3200 ppm·h at 550 °C. This is compared to the deactivation of the catalysts in the NH\(_3\)-SCR reaction, which reveals how Z-CuOH sites and Z\(_2\)-Cu sites behave in the deactivation of Cu-CHA catalysts by SO\(_2\).
Experimental
Catalyst preparation

The parent CHA zeolite powder used in this study was prepared according to a previously published procedure, which has been used in other EPR studies as well. Cu was introduced by ion-exchange of the parent H-SSZ-13 (Si/Al = 15) with an aqueous solution of Cu(CH$_3$COO)$_2$ for 24 h at 20 °C. The suspensions consisted of 1 g per 250 mL Cu(CH$_3$COO)$_2$ solution. To obtain the different Cu loadings in the Cu-CHA, the concentration of the Cu(CH$_3$COO)$_2$ solution was varied. The concentrations used for the catalysts in this study were 0.5, 1.0, 1.5, 2.0, and 5.0 mM, which resulted in Cu loadings of 0.72, 1.23, 1.63, 1.93, and 2.81 wt%, as determined by ICP-OES analysis.

SO$_2$ exposure and regeneration

To study the deactivation of Cu-CHA catalysts by SO$_2$ exposure, 0.5 g portions of the Cu-CHA with 2.81 wt% Cu were exposed to SO$_2$ for 0.5, 4, 8, 16, and 32 h at 550 °C in a quartz tube furnace. These catalyst samples are referred to as “SO$_2$ exposed”. The gas mixture used in these treatments consisted of 100 ppmv SO$_2$ and 16 % O$_2$ in N$_2$. Prior to the SO$_2$ exposure, the catalyst samples were de-greened for 1 h at 550 °C in technical air. After the exposure to SO$_2$, each catalyst portion was divided in two equal parts, and one half of each sample was regenerated in the same tube furnace at 550 °C for 5 h in a flow of 10 % O$_2$ and 3 % H$_2$O in N$_2$ at a flow rate of 200 NmL/min. These catalyst samples are referred to as “regenerated”.

NH$_3$-SCR activity measurements

The NH$_3$-SCR activities of the fresh, SO$_2$ exposed, and regenerated catalysts were determined from measurement of steady state NO conversions. For these measurements, a 5 mg sample (on a dry matter basis, sieve fraction 150-300 µm) was loaded in a fixed bed quartz reactor with an inner diameter of 2 mm. The reaction feed consisted of 500 ppmv NO, 530 ppmv NH$_3$, 10 % O$_2$ and 5 % H$_2$O in N$_2$ at a flow rate of 225 NmL/min. The concentrations of NO, NO$_2$, N$_2$O, NH$_3$ and H$_2$O were determined online, using a Gasmet CX4000 FTIR analyzer connected to the reactor outlet. For the activity measurements, the reactor temperature was stepwise increased from 160 to 550 °C and allowed to stabilize for 40 min at each temperature.

The activity of the catalysts was derived from the NO conversion as the first order rate constant, $k$, of the SCR reaction:

$$k = -\frac{F}{W\left(1 + \frac{\Delta P}{\Delta P_0}\right)}\ln(1 - X)$$

(1)
Here, $F$ is the total molar flow rate, $W$ is the dry weight of the catalyst powder, $\Delta P$ is the pressure drop over the catalyst bed, and $X$ is the fractional NO conversion. The deactivation of the catalysts is calculated as the relative loss of activity as follows:

$$\text{Deactivation} = 1 - \frac{k}{k_{fresh}}$$

**(2)**

**EPR: measurement of the total Cu content**

The EPR spectra were collected on a CW X-band Bruker EMX EPR spectrometer with an ER 4102ST cavity and a gun diode microwave source. To measure the total amount of Cu in the zeolite, the total EPR intensity of a 25 mg of the Cu-CHA sample, placed in a quartz tube, was compared to the measured intensities for a series of samples where CuSO$_4$ is diluted in K$_2$SO$_4$ to obtain a known Cu concentration in the range 0.2-5 wt%. In the fresh untreated Cu-CHA samples, the Cu is present as an EPR active hydrated form, allowing for an accurate measurement of the total Cu content.

The measurements were done within the field interval 220-400 mT, with a microwave power of 6.3 mW, a microwave frequency of 9.4-9.6 GHz, a modulation frequency of 100 kHz, and a modulation amplitude of 8 G. The spectra were collected with 2000 points and averaged over 3 scans. The Q-value was noted and carefully observed to be the same for the different samples. The EPR intensity was calculated as the double integral of the measured spectra, after background correction.

**In-situ dehydration with EPR**

For selective measurement of the Z$_2$-Cu species present in the Cu-CHA catalysts, the catalysts must be dehydrated. The dehydration was done in a flow of 50 mL/min of 20 % O$_2$ in He while heating to 250 °C at a rate of 7 °C/min, using a heater attached to the EPR cavity. The EPR spectra were continuously collected, using the parameters as given above, with a time constant of 20.48 msec and conversion time of 15 msec, which results in approximately 41-42 seconds between the start of each spectrum. A final spectrum was collected in pure He atmosphere. All spectra are background corrected by subtracting the spectrum of an empty tube and, if necessary, also by performing a linear baseline correction. The intensity of the EPR spectrum is found by double integration of the background corrected spectrum.

The EPR intensity for the dehydrated samples, $I_{rel}$, is determined by relating the EPR intensity, $I(T)$, to the intensity of the starting (fully hydrated) EPR spectrum, $I(T_{start})$, and corrected according to the Boltzmann distribution for the temperature differences according to $^{30,32}$:
EPR spectra were fitted as a sum of contributions from each Cu species. Each species is modeled using an axial spin Hamiltonian with 4 parameters, $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$. The fittings and simulations are performed using the EasySpin Toolbox in Matlab.

**Results**

**NH$_3$-SCR activity and impact of SO$_2$ exposure**

The effect of increasing SO$_2$ exposure time over Cu-CHA on the NH$_3$-SCR NO conversion is illustrated in Figure 1. Low-temperature activity (<350 °C) of the Cu-CHA catalyst is strongly reduced upon exposure to SO$_2$ (Figure 1A). The impact of SO$_2$ at temperatures above 350 °C is clearly less, indicating that deactivation by SO$_2$ is mainly relevant for the low-temperature performance, in agreement with earlier observations. The low-temperature activity after SO$_2$ exposure is partially restored by heating the Cu-CHA catalysts to 550 °C in SO$_2$-free gas (Figure 1B).

\[ I_{rel} = \frac{I(T)}{I(T_{start})} \cdot \frac{T}{T_{start}} \quad (3) \]

**Figure 1 - Steady state NO conversion of the fresh catalyst in comparison with those of A) the SO$_2$ exposed catalysts after exposure to 100 ppmv SO$_2$ and 16 % O$_2$ in N$_2$ at 550 °C for different durations, and B) the regenerated catalysts after regeneration in 10 % O$_2$ and 3 % H$_2$O in N$_2$ at 550 °C for 5 h.**
The changes in the deactivation of NH$_3$-SCR activity with time of SO$_2$ exposure are illustrated in Figure 2A, which shows the deactivation, according to Eq. 2, based on the measured NO conversion at 220 °C. About 80% of the activity is lost during the first 8 h of SO$_2$ exposure, and after 16 h of SO$_2$ exposure, the loss of activity stabilizes at 90%. This means that the deactivation of the SO$_2$ exposed catalysts does not reach 100%, but a certain NH$_3$-SCR activity, although low, is maintained even after prolonged exposure to SO$_2$. The deactivation of the regenerated catalysts increases with SO$_2$ exposure in a similar manner, reaching a maximum of 50% deactivation.

To determine the relation of the deactivation with the uptake of sulfur, the sulfur contents of the SO$_2$ exposed and regenerated catalysts were measured with ICP-OES. The measured S/Cu ratios are also included in Figure 2A. For the SO$_2$ exposed catalysts, a maximum S/Cu ratio of 0.8 is reached. The fact that the S/Cu ratio does not exceed 1 is consistent with the deactivation being related to interactions between sulfur and Cu. After regeneration at 550 °C the S/Cu ratios remain unchanged in the catalysts exposed to SO$_2$ for up to 4 h, while the S/Cu ratios drop for the catalysts subjected to longer exposures as part of the sulfur is released from the catalyst during regeneration. The highest S/Cu ratio for the regenerated catalysts is 0.5. The similar trends in the S/Cu ratio and deactivation curves in Figure 2A suggest a correlation.

Figure 2 - A) shows the deactivation (full lines) and S/Cu ratios (dashed lines) of the SO$_2$ exposed (red) and regenerated (blue) catalysts as functions of the exposure time to SO$_2$. B) shows the deactivation as function of the S/Cu ratio for the SO$_2$ exposed (red squares) and regenerated (blue circles) catalysts. The grey dashed line indicates the 1:1 correlation between the deactivation and S/Cu. The deactivation in both graphs are at 220 °C.
Figure 2B shows the deactivation as a function of the S/Cu ratios. The grey dashed line represents a 1:1 relation between the deactivation and S/Cu ratio. There is a distinct difference between the SO$_2$ exposed and regenerated catalysts: All of the SO$_2$ exposed catalysts have deactivation levels that are above the 1:1 proportionality line, whereas all of the regenerated catalysts are below the line, except for a single catalyst sample. This shows that sulfur causes a stronger deactivation before regeneration than after. This is particularly pronounced when comparing the SO$_2$ exposed and regenerated catalysts after 0.5 and 4 h of SO$_2$ exposure. In these catalysts, the deactivation levels are significantly different, but the S/Cu ratios are very similar. This shows that the regeneration is not just a consequence of the release of sulfur from the catalyst. During regeneration, the Cu,S species also changes to a form which affects the NH$_3$-SCR activity of the catalyst less. This change could be related to the sulfation of different Cu sites.$^{14,20,23}$

The sulfur also affects the activation energy for NH$_3$-SCR in a different way before and after regeneration. Figure 3 shows the apparent activation energies (190-250 °C) for the SO$_2$ exposed and regenerated catalysts as a function of the SO$_2$ exposure time. The activation energies for the SO$_2$ exposed catalysts decrease with increasing exposure time, while those of the regenerated catalysts remain stable and close to the activation energy of the fresh catalyst. This is consistent with a difference in how the sulfur interacts with the copper before and after regeneration.

![Figure 3 - Activation energies (190-250 °C) for the fresh (black), SO$_2$ exposed (red), and regenerated (blue) catalysts in the NH$_3$-SCR reaction, as function of the SO$_2$ exposure time.](image)

Recently, it was proposed that the NH$_3$-SCR activity depends on the ability of the catalyst to form Cu pairs from mobile [Cu(NH$_3$)$_2$]$^+$ species.$^{5,6}$ It was also shown that at low Cu loading, the relation between activity and Cu loading becomes quadratic because it depends on two copper sites to form the active Cu pair site, and that the activation energy increases with increasing Cu loading. In this situation, if single Cu sites were blocked, the deactivation would be disproportionately larger than the amount of affected Cu sites, as observed for the SO$_2$ exposed catalysts in Figure 2B. A part of the explanation for the observed disproportional effect of sulfur on the activity of the SO$_2$ exposed catalysts, seems likely to be related to this behavior, as well as the influence on the activation energy.

To understand the consequences of a Cu-site blocking by sulfur better, we compare in Figure 4 the activities and the apparent activation energies of the deactivated catalysts (both SO$_2$ exposed and
regenerated) to those of fresh Cu-CHA catalysts with various Cu loadings as a function of the sulfur-free Cu density. The sulfur-free Cu density was calculated as the difference between the total molar Cu content of the fresh catalyst and the total molar S content of the deactivated catalysts. The general trends of the rate constants of both the SO₂ exposed and regenerated catalysts are similar to that of the fresh catalysts, but there are some differences as well. In the higher Cu density range, the rate constants of the SO₂ exposed catalysts are slightly lower compared to the fresh catalysts. Furthermore, the rate constants for the SO₂ exposed catalysts show a quadratic dependence on the sulfur-free Cu density up to 0.44 Cu/1000 Å³. In contrast, the rate constants for the fresh catalysts only appear to follow a quadratic dependence up to about 0.33 Cu/1000 Å³. The regenerated catalysts generally show a higher rate constant than the corresponding fresh catalysts, and they do not exhibit a quadratic dependence on the sulfur-free Cu density at all.

The observed trend in the activation energy for the SO₂ exposed catalysts is similar to that of the sulfur-free catalysts. At Cu densities above 0.3 Cu/1000 Å³, the activation energy is constant around 65 kJ/mol. Below 0.3 Cu/1000 Å³, the activation energy gradually decreases to about 30 kJ/mol with Cu density. This indicates that the decrease in activity of the SO₂ exposed catalysts can be explained as a loss of active Cu. The apparent activation energies of the regenerated
catalysts do not show a decrease, but remain at a constant level of about 65 kJ/mol down to 0.22 Cu/1000 Å³. The change to higher activation energies for the samples with low effective Cu densities, after regeneration, suggests that chemical changes has occurred in the Cu phase, or that certain sites are more affected than others. Although the single site-blocking mechanism does not describe the deactivation to a full extent, it provides a useful framework to assess the deactivation behavior.

EPR results

To address the location of sulfur and possible changes in the Cu phase, catalyst samples were investigated with EPR after SO₂ exposure and regeneration. It has previously been shown that the amount of EPR active Cu in a hydrated and fresh Cu-CHA catalyst sample correlates to the total Cu amount measured by ICP. The amounts of EPR active Cu in the hydrated fresh, SO₂ exposed and regenerated catalysts were obtained by double integration of the hydrated EPR spectra (not shown). The deviations of total amounts of EPR active Cu in the SO₂ exposed and regenerated catalysts are within the expected error of quantitative EPR results, and we conclude that the SO₂ exposure and subsequent regeneration have no impact on the amount of EPR active Cu in the hydrated catalysts. Therefore, it is assumed that all samples have all Cu present as EPR active Cu when fully hydrated at room temperature.

In the dehydrated and oxidized state, Cu-CHA contains two principal Cu
²⁺ sites: one that is charge-balanced by a single framework Al and a hydroxide ion, Z-CuOH, and one that is charge balanced by two framework Al, Z₂-Cu. The EPR spectra of the dehydrated catalysts contain information about the identity and amount of Z₂-Cu sites: After in situ dehydration only the Z₂-Cu sites are EPR active, whereas any Z-CuOH sites formed are EPR silent due to 3-fold coordination around Cu. Minor species such as Cu dimers and CuₓOᵧ oligomers are also EPR silent due to magnetic coupling between Cu centers.

The EPR spectra of the fresh, SO₂ exposed, and regenerated catalysts were recorded after dehydration, and are presented in Figure 5. The total integrated intensity is collected in the two left columns of Table 2. Two sets of quartet hyperfine structure (due to interaction with the I = 3/2 Cu nuclei) are easily recognized in the parallel region of the Cu EPR spectrum and reveal the coexistence of at least 2 different Cu species. The hyperfine structure are indicated in Figure 5. All features of the EPR spectra can be simulated assuming two well-resolved Cu
²⁺ species, A1 and A2, a minority species B and an un-resolved broad species, C. The spin Hamiltonian parameters of each species are determined by simulation in Easyspin and listed in Table 1. The observed species have been identified earlier as follows. The A1 and A2 species are assigned to Z₂-Cu species in which the Cu is located near the 6 membered rings (6mr) of the CHA structure forming 4 bonds to oxygen. The B species are assigned to Cu species forming 5- or 6- bonds. Finally, the C species are assigned to a distribution of non-crystalline Cu
²⁺ species.

From Figure 5 it is seen that the signal from species C (a broad underlying feature) becomes more prominent for samples that have been exposed to SO₂ for longer time. Concurrently, the intensity of the peak related to the A1 species decrease, while the A2 species appears unchanged. A more
detailed analysis using modeling of the EPR spectra is carried out in order to follow the individual species more quantitatively. Therefore, each spectrum was fitted as a linear combination of the 4 species A1, A2, B and C.

![EPR spectra](image)

**Figure 5** - EPR spectra recorded at 25 °C in a flow of He after in-situ dehydration of SO$_2$ exposed and regenerated Cu-CHA samples. The parallel region of the EPR spectra are expanded in the inset where the quartet hyperfine pattern of the two most well-defined Cu species, A1 and A2 are indicated.

**Table 1** - Fitted spin Hamiltonian parameters of different Cu species from the EPR spectra in Figure 5.

<table>
<thead>
<tr>
<th>Species</th>
<th>Spin Hamiltonian Parameters</th>
<th>Line width (FWHM in MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_\parallel$</td>
<td>$g_\perp$</td>
</tr>
<tr>
<td>A1</td>
<td>2.32</td>
<td>2.07</td>
</tr>
<tr>
<td>A2</td>
<td>2.36</td>
<td>2.07</td>
</tr>
<tr>
<td>B</td>
<td>2.26</td>
<td>2.09</td>
</tr>
<tr>
<td>C</td>
<td>$g = 2.16$</td>
<td></td>
</tr>
</tbody>
</table>

*These were not well resolved and are based on estimations

The fitted intensity of each Cu$^{II}$ species were related to the corresponding total EPR intensity of the hydrated catalysts that reflect the total Cu content. Thus, the fractions of the four different Cu$^{II}$
species relative to the total Cu content in each SO₂ exposed and regenerated catalyst were estimated and are listed in Table 2 and graphically displayed in Figure 6.

Table 2 - Intensities of EPR active Cu after dehydration in the fresh, SO₂ exposed and regenerated catalysts. The distributions of EPR active Cu species (A1, A2, B and C) from fittings to the raw EPR spectra after dehydration are also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>EPR intensity after dehydration (%)</th>
<th>Distribution of EPR active Cu* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO₂ exposed</td>
<td>Regenerated</td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>A2</td>
</tr>
<tr>
<td>Fresh</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>0.5 h</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>4 h</td>
<td>42</td>
<td>43</td>
</tr>
<tr>
<td>8 h</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>16 h</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>32 h</td>
<td>58</td>
<td>55</td>
</tr>
</tbody>
</table>

*calculated as the amount of Cu in that particular species out of the total Cu content using the amount of EPR active Cu before dehydration.

As seen in Figure 6, the total amount of EPR active Cu in the dehydrated spectra (the sum of the four different CuⅡspecies) increases with SO₂ exposure time, from initially 38% of the total Cu content to about 57%. The amounts of A1 and B species slightly decrease, and the amount of A2 species remains constant. The decrease of A1 and B species occurs in parallel to the increase of the C species. However, the total decrease in A1 and B species, i.e. from approx. 19% to 9%, is less than the increase of C species. Therefore, the increase of C, at least partially, has to arise from EPR silent Cu species becoming EPR active after the exposure to SO₂. This is an indirect indication that SO₂ interacts with the EPR silent Z-CuOH species. This is corroborated by comparing the S/Cu ratios in Figure 2, with the EPR results of the catalysts exposed to SO₂ for 16 and 32 h. The S/Cu ratios are 0.8 while the sulfur-free A1 and A2 Cu species constitute about 20% of the total Cu content, again implying that sulfur is associated with the EPR silent Z-CuOH sites leading to the C species.

The amount of Cu in the Z₂ positions (A1 and A2 combined) decreases with SO₂ exposure time, and stabilize around 8 h of SO₂ exposure. From Figure 2A it can be seen that the S/Cu ratio follows the inverse trend. After regeneration of the catalyst, the S/Cu ratio drops from 0.8 to 0.5, while there are no major changes to the EPR active Cu. This indicates that primarily sulfur associated with the Z-CuOH sites is released during regeneration.

The A2 species in both the SO₂ exposed and regenerated catalysts remain at a constant level of about 15% for all exposure times, indicating that this Cu species is not affected by the SO₂ exposure. This is also consistent with the S/Cu ratio not exceeding 0.8, as seen in Figure 2, and is a possible explanation why a complete deactivation is never observed, even after prolonged SO₂ exposures.¹⁵

There is an interesting development of the A1 and C species when comparing the SO₂ exposed and regenerated catalysts exposed to SO₂ for 0.5 h and 4 h. The EPR measurements show that the
amount of the A1 species are constant up to 4 h of SO$_2$ exposure, but after regeneration the amount of A1 species has dropped, which occurs in parallel to an increase of the C species. The corresponding S/Cu ratios measured with ICP (Figure 2) are similar for the SO$_2$ exposed and regenerated catalysts, implying that sulfur is not removed during regeneration. This indicates that a relocation of sulfur, or Cu,S species, is taking place during regeneration. Such a relocation may also occur during SO$_2$ exposure, as indicated by the similar amounts of A1 species that are present after 4 h of SO$_2$ exposure + 5 h of regeneration (effectively 9 h at 550 °C) and after 8 h of SO$_2$ exposure at 550 °C.

![Figure 6 - Fractions of Cu species A1, A2, B and C relative to the total Cu content of the catalysts, plotted as function of the SO$_2$ exposure time. The values are determined by analysis of the EPR spectra in Figure 5 in the SO$_2$ exposed (solid lines with full symbols) and regenerated (dashed lines with open symbols) catalysts.](image)

**Discussion**

In accordance with previous reports, the molar S/Cu ratios presented in Figure 2 do not exceed 1. This supports the conclusion that the SO$_2$ interacts with the Cu sites to form Cu$_x$S species. Density Functional Theory calculations show a clear difference in reactivity of the Z$_2$-Cu in the 6-membered ring and the Z-CuOH species towards SO$_2$ and SO$_3$. According to these calculations, SO$_2$ and SO$_3$ form stable Cu$_x$S species on Z-CuOH sites, but do not adsorb on Z$_2$-Cu in the 6-membered ring. This agrees with our EPR results for the A2 species, which are not influenced by SO$_2$. The A1 species is also assigned as a Z$_2$-Cu site, but with another local distribution of Al.
The evidence points to the fact that sulfur interacts to some extent with this species. Also, A1 was previously shown to be more reactive than the A2 species, and this is further demonstrated here. There is the possibility that water plays a role in the interaction of SO\textsubscript{2} with Z\textsubscript{2}-Cu and this is enough to activate the A1 species but not the A2 species. Presence of trace water during the SO\textsubscript{2} exposure is likely, and the regeneration was carried out in the presence of water, while the presence of water was not accounted for in the DFT calculations. In line with the DFT calculations, the EPR data also indicate that SO\textsubscript{2} preferably interacts with the Z-CuOH species.

As argued in the results section, a relocation of sulfur or Cu,S species occurs at extended exposure to 550 °C. This relocation appears to be part of a kinetically limited reaction, which leads to more C species, which are argued to be Cu,S that are stable at 550 °C. Such stable Cu,S species in Cu-CHA catalysts are described as certain Cu sulfates. Thus, it is plausible that the kinetically limited reaction is an oxidation reaction of SO\textsubscript{2} to SO\textsubscript{3}, consistent with TGA measurements, that involves a relocation of sulfur or Cu,S species, and leads to formation of the “irreversible” Cu,S species.

The EPR results presented in Figure 6 shows that the Z\textsubscript{2}-Cu sites are largely unaffected by SO\textsubscript{2} exposure and regeneration, constituting about 30% of the total Cu in the fresh catalyst and about 20% after 32 h of SO\textsubscript{2} exposure. Simultaneously, the ICP measurements in Figure 2 reveal that S/Cu ratios as high as 0.8 are reached after SO\textsubscript{2} exposure, which then drops to 0.5 after regeneration. Indirectly, this shows that predominantly the Z-CuOH sites are associated with sulfur after SO\textsubscript{2} exposure, and that the regeneration in SO\textsubscript{2}-free gas mainly liberates the Z-CuOH sites from sulfur by desorption or relocation. The concurrent kinetic measurements show that after SO\textsubscript{2} exposure, the apparent activation energies are lowered, and that subsequent regeneration restores the apparent activation energies to the same level as that of the fresh catalyst.

We now put these observations in context with the current understanding of the low-temperature SCR mechanism over Cu-CHA catalysts. The activation energy increases with Cu loading, as shown in Figure 4B. At high Cu loadings and activation energies, the SCR reaction is limited by O\textsubscript{2} dissociation on Cu pairs that are formed by mobile [Cu(NH\textsubscript{3})\textsubscript{2}]+ complexes. At low Cu loadings and activation energies, the reaction is limited by the formation of Cu pairs. Applying this understanding on the SO\textsubscript{2} exposed catalysts, it suggests that the blocking of Z-CuOH sites by sulfur limits the ability of the catalyst to form Cu pairs. This then leads to the lower activation energies of the SO\textsubscript{2} exposed catalysts and the quadratic dependence of the SCR activity of the SO\textsubscript{2} exposed catalysts on the amount of sulfur-free Cu (Figure 4A). In the regenerated catalysts, where mainly the Z-CuOH sites have released the sulfur, the activation energies are back at the same level as in the fresh catalyst, where O\textsubscript{2} dissociation limits the SCR activity. Therefore, the ability to form Cu pairs appears to be unaffected in the regenerated catalysts, while this ability is noticeably hindered in the SO\textsubscript{2} exposed catalysts with the same exposure to SO\textsubscript{2}. This implies that the ability of Cu-CHA catalysts to form Cu pairs depends on the Z-CuOH sites. The observed differences between the impacts of sulfur in the SO\textsubscript{2} exposed and regenerated catalysts, on the overall NH\textsubscript{3}-SCR activity, therefore, appear to be linked to the selective deactivation of the Z-CuOH sites and the significance of these sites for Cu pair formation.
Conclusions

The impact of SO\(_2\) on the catalytic performance of a Cu-CHA catalyst in the NH\(_3\)-SCR reaction was studied. Exposure of a Cu-CHA catalyst to 100 ppmv SO\(_2\) at 550 °C, for up to 32 h, results in deactivation that increases with exposure time up to a limit of 90%, which is accompanied by a parallel sulfur uptake reaching a maximum S/Cu ratio of 0.8. Consistently, characterization with electron paramagnetic resonance (EPR) spectroscopy showed that certain Z\(_2\)-Cu sites, associated with 2 Al centers, were unaffected by sulfur, which added up to about 15% of the total Cu content.

Regeneration at 550 °C in SO\(_2\)-free gas lowers the maximum deactivation to 50% and the S/Cu ratio to 0.5. Generally, the impact of sulfur on the activity is higher in the SO\(_2\) exposed catalysts, compared to the regenerated catalysts.

The rate constants and apparent activation energies of the SO\(_2\) exposed catalysts in the NH\(_3\)-SCR reaction have a similar dependence on the sulfur-free Cu density as fresh Cu-CHA catalysts with different Cu loadings, indicative of a site-blocking deactivation mechanism.

Parallel measurements with EPR showed that SO\(_2\) mainly interacts with Z-CuOH sites, associated with a single Al center, before regeneration. During regeneration, the Z-CuOH sites are liberated from sulfur by desorption and relocation. The relocation of sulfur or Cu,S species is likely part of the formation of more stable Cu,S species via a kinetically limited oxidation of SO\(_2\).

The preference of sulfur adsorption on Z-CuOH sites before regeneration, and the associated lowering of the apparent activation energy, indicates that the Z-CuOH are more important for Cu pair formation in the Cu-CHA catalysts, compared to Z\(_2\)-Cu sites.

References

Chapter 6


Chapter 6
Chapter 7

Introducing Temperature-Programmed Reduction with NO as a new characterization of active Cu in Cu-CHA catalysts for NH₃-SCR
Abstract
To measure active Cu in Cu-CHA catalysts for selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR), we introduce temperature-programmed reduction with NO (NO-TPR) as a new method. In NO-TPR, the NO consumption is measured in the reduction as it occurs in NH\textsubscript{3}-SCR. reaction (NO+NH\textsubscript{3}) during reduction of an oxidized Cu-CHA catalyst. The reduction shows NO consumption features at 130 and 230 °C, associated with a Cu-oxide phase and Cu-nitrate phase, respectively. For catalysts with high Cu loadings, the NO consumption at 230 °C is exactly 3 times larger than the Cu content measured with ICP, consistent with the reduction of Cu-nitrate in NH\textsubscript{3}-SCR. In catalysts with low Cu loading, not all Cu forms a stable Cu-nitrate. The NH\textsubscript{3}-SCR activity appears to be related with the ability to form stable Cu-nitrate. The NO-TPR method was also directly applicable to SO\textsubscript{2} exposed Cu-CHA catalysts after regeneration, while the Cu,S species before regeneration were too unstable to make a consistent measurement.

Introduction
The catalytic properties of chabazite zeolite ion-exchanged with Cu (Cu-CHA) have been studied extensively during the past decade [1–5]. The Cu-CHA typically have a Si/Al ratio in the range 5-20, and the excess charge of the zeolite is compensated by H\textsuperscript{+} and Cu ions. The Cu ions have the ability to change the oxidation state between Cu\textsuperscript{I} and Cu\textsuperscript{II}, dependent on the gas atmosphere and temperature [6], which implies that these ions have specific redox properties that can be exploited for catalysis.

One of the most studied reactions catalyzed by Cu-CHA is the selective catalytic reduction of NO with ammonia in the presence of oxygen (NH\textsubscript{3}-SCR) [1–4,7]. For NH\textsubscript{3}-SCR, Cu-CHA materials are very efficient and robust catalysts, with both a high activity at around 200 °C, and a high hydrothermal stability up to about 700 °C. These materials are, therefore, well suited for application in automotive diesel exhaust aftertreatment systems, and are already applied today in heavy-duty vehicles. The Cu-CHA catalyst makes it possible to meet the latest requirements (e.g. Euro 6/VI) for NO\textsubscript{x} (NO and NO\textsubscript{2}) emissions from diesel engines [8].

The reduction of NO in the NH\textsubscript{3}-SCR reaction follow the reaction 4 NO + 4 NH\textsubscript{3} + O\textsubscript{2} → 4 N\textsubscript{2} + 6 H\textsubscript{2}O; this reaction is often called the 'standard-SCR' reaction. In recent years, significant progress has been made in understanding the reaction mechanism [4,6,7,9–13]. The NH\textsubscript{3}-SCR reaction cycle can be performed in steps on Cu-zeolite catalysts, by alternating the oxidation and reduction steps [6,9–11,14,15]. In the reduction step, the Cu starts in the Cu\textsuperscript{II} state and is reduced to Cu\textsuperscript{I} in a mixture of NO and NH\textsubscript{3}, and, dependent on the conditions, a Cu(NH\textsubscript{3})\textsuperscript{2+}-complex is formed. In the oxidation part, this Cu\textsuperscript{I} is reoxidized to a Cu\textsuperscript{II} species by a reaction with an NO/O\textsubscript{2} mixture.

The oxidation part of the standard NH\textsubscript{3}-SCR reaction involves the dissociation of molecular oxygen, and in the presence of NO, a Cu-nitrate is formed [9,16,17]. According to DFT calculations, molecular oxygen is expected to adsorb exclusively on a Cu\textsuperscript{I} species [9], which implies that a Cu\textsuperscript{II} species does not contribute to the activation of O\textsubscript{2}. The simplest scenario of oxygen dissociation on a Cu ion is then that an oxygen molecule adsorbs on a single Cu ion, where it dissociates. In the presence of NO, this seems a possible reaction path [9,18].
If the $\text{O}_2$ molecule can interact with two $\text{Cu}^{1+}$-ions simultaneously, to form a $\text{Cu-O}_2$-$\text{Cu}$ type of species, the dissociation of the $\text{O}_2$ becomes easier [10]. The activation of oxygen over a pair of Cu ions seems to be relevant for the $\text{NH}_3$-SCR reaction at low temperatures [10,11]. Under these reaction conditions, the $\text{Cu}^{1}$ species is present as a linear $\text{Cu(NH}_3)_2^{2+}$-complex [6,10,14,19], and DFT calculations indicate that direct dissociation of an $\text{O}_2$ molecule on a single $\text{Cu(NH}_3)_2^{2+}$-complex does not occur [11,20]. The observation that the rate of oxidation of $\text{Cu(NH}_3)_2^{2+}$-complexes in a CHA zeolite with $\text{O}_2$ shows a second order dependence on Cu-concentration further supports the conclusion that the oxidation of $\text{Cu(NH}_3)_2^{2+}$-complexes in a Cu-zeolite involves pairs of $\text{Cu(NH}_3)_2^{2+}$-complexes [10,11]. The presence of NO also seems to enhance the activation of $\text{O}_2$ on pairs of bare $\text{Cu}^{1+}$ ions or $\text{Cu(NH}_3)_2^{2+}$-complexes [20].

An obvious way to form pairs of Cu ions that interact with a single $\text{O}_2$ molecule is by having two Cu ions in positions close enough for a direct interaction with a single $\text{O}_2$ molecule. Since the Cu ions in the ion-exchange positions in a zeolite are linked to the aluminium atoms, the ability to form Cu pairs increases with decreasing Si/Al ratio in the zeolite. This is part of the explanation why Cu-zeolites with a Si/Al ratio in the range 5-20, are generally the preferred catalysts for the $\text{NH}_3$-SCR reaction.

The mobility of the $\text{Cu(NH}_3)_2^{2+}$-complex is another way to form the Cu pairs that can activate the $\text{O}_2$ molecule. For Cu-CHA, it has been shown that the $\text{Cu(NH}_3)_2^{2+}$-complex has a weak interaction to the zeolite framework [21], and can move up to about 9 Å away from its Si-O-Al anchor point in the zeolite framework [10]. This means that the actual active sites for $\text{O}_2$ activation in $\text{NH}_3$-SCR are formed dynamically under the influence of the $\text{NH}_3$-SCR conditions that are necessary to form the $\text{Cu(NH}_3)_2^{2+}$-complex. A consequence is that the $\text{NH}_3$-SCR reaction necessarily follows a different mechanism at temperatures where the mobile $\text{Cu(NH}_3)_2^{2+}$ complex is stable and where it is not. This change in the reaction mechanism has been proposed as the reason for the decrease in SCR rate with increasing temperature [9–12,19], which is characteristic for Cu-CHA catalysts and occurs around 300 °C for Cu-CHA catalysts, in good agreement with the measurement of the thermal stability of the $\text{Cu(NH}_3)_2^{2+}$-complex [19].

The mobility of the Cu and dynamic formation of the active centers in a Cu-CHA catalyst implies that characterization of the Cu-CHA materials not necessarily gives information that is relevant for the $\text{NH}_3$-SCR reaction. In this chapter, we present temperature-programmed reduction with NO (NO-TPR) as a new method for exploring the reduction and oxidation properties of active Cu in Cu-CHA materials that are relevant for $\text{NH}_3$-SCR. The NO-TPR procedure is based on the ability to perform the $\text{NH}_3$-SCR reaction in alternating oxidation and reduction steps. It has been shown that the reduction of Cu in the $\text{NH}_3$-SCR reaction requires the presence of both $\text{NH}_3$ and NO. By following the consumption of NO under controlled heating, the reduction properties of the Cu in the Cu-CHA catalysts are revealed. Reduction properties of Cu-CHA catalysts have been studied earlier with $\text{H}_2$-TPR [6,22–25], as a method to study the redox properties of Cu-CHA catalysts. Even though the reduction of Cu with $\text{H}_2$ gives some information about the oxidation state of the Cu-CHA materials, and amount of Cu present, these properties cannot necessarily be related to the $\text{NH}_3$-SCR reaction. Since the reduction in a mixture of NO and $\text{NH}_3$ is also part of the $\text{NH}_3$-SCR reaction itself, the reduction as observed in NO-TPR directly reflects the reduction of the active Cu species as it occurs in the $\text{NH}_3$-SCR reaction.
In this chapter, we develop and explore the NO-TPR method in a study of the redox properties for a series of Cu-CHA catalysts with different Cu loadings on the same parent CHA material (Si/Al = 15). The reduction properties of these catalysts are characterized by NO-TPR and we show how the reduction properties of Cu-CHA change with Cu loading. The low-temperature activity at 200 °C of the Cu-CHA catalysts is related to the reduction properties of the Cu-CHA catalysts. Furthermore, the low-temperature activity correlates to the ability of forming stable Cu(NO₃) species, which is affected by the Cu loading. This provides a new possible way of measuring active Cu in Cu-CHA catalysts, as well as a new insight in the NH₃-SCR activity of Cu-CHA catalysts with different Cu loading.

The ability to measure the active Cu, and assess the reduction properties in an SCR related gas composition, is also relevant for studying the deactivation of Cu-CHA catalysts by SO₂. As elaborated in Chapters 2-6, the deactivation by SO₂ is tightly associated with the formation of different Cu,S species. So far, it has only been possible to relate the sulfur in the catalysts to the total Cu content and to the impact on the activity. Important areas for developing a better understanding of the deactivation, is therefore, to ascertain the amount of active Cu sites that are affected by sulfur, and to realize how the sulfur affects the chemistry of the active Cu sites in relation to the SCR reaction mechanism. In this respect, the NO-TPR method could prove a useful tool. Therefore, we also explore the applicability of the NO-TPR method on SO₂-exposed Cu-CHA catalyst before and after regeneration in this chapter. We show that NO-TPR in the current form is directly applicable on the regenerated catalysts, while it still may require adjustments for the sulfated catalysts.

**Experimental**

**NO-TPR: Catalysts**

The catalysts used for the development of the NO-TPR method is a series of six Cu-CHA catalysts with Si/Al = 15.1 and a Cu loading ranging from 0.7 to 3.1 wt% Cu. Table 1 gives a more detailed overview of the catalysts. The Cu content, as measured by ICP, was corrected with the measured dry matter content of the catalyst to obtain the Cu content with respect to the amount of dry zeolite. The dry matter content of the catalysts was determined from measurement of the weight loss upon heating to 200 °C, using a Mettler Toledo HX204 moisture analyzer. The Cu/Al ratio is calculated on the basis of the Cu-content on a dry-matter basis and the known Si/Al ratio of 15.1 of the parent material, under the assumption that the Si is present as SiO₂, Al is present as AlO₂H, and Cu is present as CuO. The Cu/Al ratio is then given by

\[
\frac{N_{Cu}}{N_{Al}} = \frac{x_{Cu} \left( \frac{N_{Si}}{N_{Al}} M_{SiO_2} + M_{AlO_2H} \right)}{M_{Cu} - x_{Cu} M_{CuO}}
\]

(1)

where \(N_{Si}, N_{Al}\) and \(N_{Cu}\) are the molar amounts of Si, Al, and Cu atoms, \(x_{Cu}\) is the weight fraction of Cu on a dry-zeolite basis, and \(M\) indicates the molar mass for a unit of SiO₂, AlO₂H, Cu, or CuO.
Table 1 - Measured Cu content by ICP and dry matter content, Si/Al ratio and the corresponding Cu/Al ratio and Cu content on dry matter basis for the catalysts used.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu content ICP</th>
<th>Dry matter</th>
<th>Si/Al</th>
<th>Cu/Al</th>
<th>Cu content (dry matter basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>wt%</td>
<td></td>
<td></td>
<td>wt%</td>
</tr>
<tr>
<td>A</td>
<td>0.717</td>
<td>89.7</td>
<td>15.1</td>
<td>0.123</td>
<td>0.799</td>
</tr>
<tr>
<td>B</td>
<td>1.232</td>
<td>90.7</td>
<td>15.1</td>
<td>0.210</td>
<td>1.358</td>
</tr>
<tr>
<td>C</td>
<td>1.629</td>
<td>89.4</td>
<td>15.1</td>
<td>0.284</td>
<td>1.822</td>
</tr>
<tr>
<td>D</td>
<td>1.930</td>
<td>91.9</td>
<td>15.1</td>
<td>0.328</td>
<td>2.100</td>
</tr>
<tr>
<td>E</td>
<td>2.625</td>
<td>91.5</td>
<td>15.1</td>
<td>0.453</td>
<td>2.869</td>
</tr>
<tr>
<td>F</td>
<td>3.142</td>
<td>90.4</td>
<td>15.1</td>
<td>0.554</td>
<td>3.476</td>
</tr>
</tbody>
</table>

Reactor setup for NH$_3$-SCR activity and NO-TPR measurements

The NH$_3$-SCR activity of the Cu-CHA catalysts and NO-TPR measurements were done in a microreactor setup for powder samples, in which the reactor is mounted via a 4-way valve that allows for bypassing the reactor. The concentrations of NO, NO$_2$, N$_2$O, H$_2$O, and NH$_3$ are monitored with an FTIR spectrometer (Gasmet CX4000) at the reactor outlet; the composition of the feed gas is measured by bypassing the reactor.

For the activity measurement, a 5 mg sample (based on dry matter, sieve fraction 150-300 µm) of the catalysts was filled into a quartz U-tube reactor with an inner diameter of 2 mm. Before starting the measurements, the catalysts were heated at 550 °C in 10% O$_2$/N$_2$ for 1 h. Then, the feed gas was changed to 225 Nml/min NH$_3$-SCR feed gas, consisting of 500 ppm NO, 533 ppm NH$_3$, 5% water, 10% O$_2$, and balance nitrogen. The temperature was stepwise lowered to 500, 450, 400, 350, 300, 280, 250, 230, 220, 210, 200, 190, 180, 170, and 160 °C, and at each temperature, the system was allowed to stabilize for 20 min. To evaluate the NH$_3$-SCR activity, the rate constant for NH$_3$-SCR at 200 °C is determined from the measured conversion of NO at that temperature, under the assumption that the NH$_3$-SCR reaction is first order in NO. The rate constant is then given by:

$$k_{200} = \frac{F}{W} \ln(1 - X)$$

(2)

For the NO-TPR measurements, a catalyst powder sample of about 50 or 100 mg on a dry matter basis (150-300 µm sieve fraction) in a quartz U-tube reactor with an inner diameter of 4 mm was used. Various procedures were used for the NO-TPR measurements, which are explained in more detail below.

SO$_2$-exposed Cu-CHA materials

To determine whether the NO-TPR method can be used to monitor the deactivation of Cu-CHA catalysts by SO$_2$, the NO-TPR method was applied to some of the SO$_2$ exposed and regenerated
Cu-CHA catalysts that were made for the investigations of the lifetime impact of SO\textsubscript{2}, described in Chapter 5. The specific catalysts that were subjected to NO-TPR are the fresh Cu-CHA (Si/Al = 14.6, ICP: 2.43 wt% Cu), the SO\textsubscript{2} exposed and the regenerated catalyst samples that had been exposed to SO\textsubscript{2} for 1, 5, 15, and 65 h at 300 °C. Detailed information about the SO\textsubscript{2} exposure and regeneration conditions are given in Chapter 5. These catalyst samples were chosen because they contain different amounts of sulfur and show different degrees of deactivation.

**NO-TPR Method**

It has been shown earlier, that the NH\textsubscript{3}-SCR reaction cycle over Cu-zeolite catalysts can be executed by alternating oxidation and reduction steps [9,13]. In the oxidation step, the Cu-zeolite catalyst is exposed to a mixture of NO and O\textsubscript{2}, and the Cu is brought into the Cu\textsuperscript{II} oxidation state. Characterization of this Cu\textsuperscript{II} phase by FTIR, XAS, and EPR indicate that a Cu-nitrate species is formed [9,16,17,26,27]. The reduction part of the NH\textsubscript{3}-SCR reaction takes place upon exposure of this Cu\textsuperscript{II} state to a mixture of NO and NH\textsubscript{3}, and results in the formation of a Cu\textsuperscript{I} state, which is a Cu(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+} complex at sufficiently low temperature [7,11,19]. Reoxidation of the reduced Cu\textsuperscript{I} state with a mixture of NO and O\textsubscript{2} results in the original Cu\textsuperscript{II} state.

The basic idea of the NO-TPR experiments is to exploit the possibility of performing the NH\textsubscript{3}-SCR reaction in two steps. In the first part, an oxidized state of the Cu in the catalyst is prepared, which typically, but not necessarily, involves exposure of the catalyst to a mixture of NO and O\textsubscript{2}. The reduction step is done by heating the catalyst at a predefined rate in a mixture of NO and NH\textsubscript{3}, while following the NO and NH\textsubscript{3} concentrations to give the NO-TPR data. The consumption of NH\textsubscript{3} due to reduction of the Cu is obscured by adsorption and desorption of NH\textsubscript{3} on the zeolite, and hence, it is difficult to obtain reliable quantitative data on the reduction of the Cu from the measured NH\textsubscript{3} consumption. In contrast, NO interacts weakly with the zeolite, and therefore, the reduction of the Cu is clearly observed in the consumption of the NO during reduction.

To ensure a well-defined state of the catalyst in the NO-TPR, the experimental procedure consists of three parts, namely:

1. the preparation of the Cu\textsuperscript{II} state.
2. equilibrating the Cu\textsuperscript{II} state in a mixture of NH\textsubscript{3} and NO at 50 °C, the start temperature for the temperature ramp.
3. heating of the catalyst sample in the mixture of NH\textsubscript{3} and NO to 370 °C with 3°C/min at a flow of 200 Nml/min.

Variations in the preparation of the Cu\textsuperscript{II} state are possible, and this actually affects the final consumption of NO in the NO-TPR. For the NO-TPR data presented here, the exposure to the NO/O\textsubscript{2} mixture is preceded by a reduction step in NO/NH\textsubscript{3} at 200 °C or by an oxidation in O\textsubscript{2} at 500 °C.

We have chosen to start the reduction at 50 °C, which is the lowest practical temperature that can be achieved in our equipment. Since the NH\textsubscript{3}-SCR reaction, and therefore also the reduction in the NO/NH\textsubscript{3} mixture, is already very effective at 200 °C, the reduction must be started at a significantly lower temperature, in order to detect the NO consumption during reduction. To achieve a well-defined and reproducible state of the catalyst before heating the catalyst, the Cu\textsuperscript{II} state is
equilibrated at 50 °C until the adsorption of NH$_3$ on the zeolite is completed, and the measured concentrations of NO and NH$_3$ correspond to the inlet concentrations.

Figure 1 gives an overview of the concentrations of NO, NO$_2$, N$_2$O, NH$_3$ and O$_2$ during the entire procedure for NO-TPR, using 55 mg of catalyst E. The shaded areas indicate the steps in the pretreatment of the catalyst, viz. heating to 500 °C, reduction in NH$_3$/NO at 200 °C, oxidation in O$_2$/NO at 50 °C to prepare the Cu$^{II}$ state, exposure to NH$_3$/NO at 50 °C to equilibrate, and finally the TPR step in NO/NH$_3$ during heating to 370 °C. Before each step, the reactor was bypassed to mix the feed gas to the appropriate concentration, and to measure the composition of the feed gas at each stage. The analysis of the reduction of the Cu-CHA catalysts is based on the consumption of NO during heating to 370 °C (blue curve in red shaded area).

![Figure 1](image_url)

*Figure 1 - Concentrations of NO, NH$_3$, NO$_2$, N$_2$O, O$_2$ and temperature during the entire procedure for an NO-TPR measurement.*

Before turning our attention to the analysis of the actual NO-TPR data, we first discuss a few observations that occur during the different reduction and oxidation steps before the actual reduction is done. When the NO/NH$_3$ mixture is admitted to the reactor at 200 °C in the reduction step, some NO is consumed, indicating that the Cu is in an oxidized state after heating to 500 °C in O$_2$. Simultaneously, a much larger amount of NH$_3$ is consumed, even though the reduction of Cu$^{II}$ to Cu$^{I}$ requires equimolar amounts of NO and NH$_3$. The reasons for the larger consumption
of \(\text{NH}_3\), compared to \(\text{NO}\), is that additional \(\text{NH}_3\) is used for the formation of the linear \(\text{Cu}(\text{NH}_3)_2^+\) complex and that \(\text{NH}_3\) adsorbs on the Brønsted sites in the zeolite at 200 °C.

After the reduction at 200 °C, in which the linear \(\text{Cu}(\text{NH}_3)_2^+\) complex is formed, the catalysts are oxidized at 50 °C in a mixture of 2000 ppm \(\text{NO}\) and 10 % \(\text{O}_2\), which yields a \(\text{Cu}^{\text{II}}-(\text{N,O})\) phase. Figure 1 shows that about 60 ppm \(\text{NO}_2\) is formed in this mixture while bypassing the reactor, due to the gas phase oxidation of \(\text{NO}\) that occurs in the mixture. Exposing the reduced catalyst to this \(\text{NO/O}_2\) at 50 °C mixture leads to a further oxidation of \(\text{NO}\), to yield approximately 160 ppm of \(\text{NO}_2\), due to the known oxidation of \(\text{NO}\) to \(\text{NO}_2\) in the confined spaces of the zeolite [28]. For this work, it is important to note that some \(\text{NO}_2\) has been present during this oxidation step, but we do not address this formation of \(\text{NO}_2\) further. The presence of \(\text{NO}_2\) results in a complete oxidation of the \(\text{Cu}(\text{NH}_3)_2^+\) complex, without residual \(\text{Cu}^\text{I}\) phase [10]. Spectroscopic analysis using FTIR, EPR, and XANES has shown that a \(\text{Cu(NO}_3)\) phase is formed upon oxidation of the \(\text{Cu}(\text{NH}_3)_2^+\)-complex with \(\text{NO}_2\) or in a mixture of \(\text{NO}\) and \(\text{O}_2\) [9,16,29,30]. We will present further evidence that \(\text{Cu(NO}_3)\) probably is the major constituent of the \(\text{Cu}^{\text{II}}-(\text{N,O})\) phase formed at 50 °C in this procedure [16].

Finally, before the TPR run can be started, the oxidized \(\text{Cu}^{\text{II}}-(\text{N,O})\) phase must be exposed to the mixture of \(\text{NO}\) and \(\text{NH}_3\) at 50 °C. The ammonia adsorption that occurs under these conditions leads to the delayed breakthrough of the ammonia. Furthermore, a small amount of \(\text{NO}\) is consumed initially, together with a larger release of \(\text{NO}_2\). This shows that at least a part of the \(\text{Cu}^{\text{II}}-(\text{N,O})\) phase reacts with \(\text{NO}\) and possibly also with \(\text{NH}_3\), already at 50 °C, indicating that already at 50 °C, the \(\text{Cu}^{\text{II}}-(\text{N,O})\) species reacts with \(\text{NH}_3\) and \(\text{NO}\). The release of \(\text{NO}_2\), however, is not compatible with a complete \(\text{NH}_3\)-SCR reaction, which only produces \(\text{N}_2\) and \(\text{H}_2\text{O}\). It may indicate the reaction between a Cu-nitrate species and \(\text{NO}\), which can release \(\text{NO}_2\) into the gas phase while forming Cu-nitrite; this reaction would not change the oxidation state of the Cu [9].

**Results**

Figure 2 shows a series of NO-TPR data for the series of Cu-CHA catalysts A-F with different Cu-loading, as specified in Table 1. All data were obtained using the procedure as shown in Figure 1, which means that the \(\text{Cu}^{\text{II}}-(\text{N,O})\) phase is formed in a reaction of \(\text{Cu}^\text{II}\) (possibly \(\text{Cu}(\text{NH}_3)_2^+\)) with the \(\text{NO/O}_2\) mixture. The reduction was done by heating to 370 °C at a rate of 3 °C/min in a mixture of 800 ppm \(\text{NO}\) and 900 ppm \(\text{NH}_3\) with 200 Nml/min.

The data in Figure 2 show two distinct temperature ranges for NO consumption for the catalysts with a low Cu loading, with maximum consumptions at around 130 °C and 230 °C. At higher Cu loadings, the NO consumption at around 130 °C is not present, and the peak at 230 °C widens towards the low temperature side, with the maximum NO consumption shifting to just below 200 °C. The disappearance of the NO consumption around 130 °C with increasing Cu loading is highlighted in the right panel of Figure 2, clearly showing the change in the shape of the TPR profile with increasing Cu loading. The total area under the curves increases with Cu loading, which is in line with the expectation that more NO is consumed when more Cu is present. The two distinct regions where NO consumption takes place indicate that there are at least two different forms of oxidized Cu that are reduced in the mixture of \(\text{NO}\) and \(\text{NH}_3\); we designate the Cu species associated with the peak around 130 °C and 230 °C as Cu-\(a\) and Cu-b, respectively.
In the following, we show that Cu-\(a\) is a Cu\(\text{II}\) species that does not contain nitrogen, and that Cu-\(b\) is a Cu(NO\(3\)) species. This assignment is made on the basis of additional NO-TPR measurements, in which the procedure for the formation of the Cu\(\text{II}\) species has been varied, and a further analysis of the NO-TPR data presented in Figure 2.

The two features corresponding to the Cu-\(a\) and Cu-\(b\) species obtained after exposure of the reduced Cu to the O\(2\)/NO mixture on catalyst B are also shown in Figure 3. Furthermore, omitting the exposure to O\(2\)/NO, Figure 3 shows that there is no significant NO consumption over catalyst B. This is expected, since the catalyst has not been oxidized after the initial reduction at 200 °C, leaving the catalyst in the reduced state when performing the NO-TPR measurement.

Figure 3 also presents NO-TPR curves for catalysts B and D, which were measured with and without exposure to the NO/O\(2\) mixture at 50 °C, after oxidation of the Cu at 500 °C in O\(2\). The NO-TPR profiles change when an oxidized catalyst is exposed to the NO/O\(2\) mixture. Heating of the Cu-CHA catalyst to 500 °C in O\(2\) results in the formation of Cu\(\text{II}\) species [5,6]. Exposure of this Cu\(\text{II}\) species to the NO/O\(2\) mixture at 50 °C results in a peak around 120 °C, and a peak around 230 °C in the NO-TPR profile. At low Cu loadings (catalyst B, 1.35 wt% Cu), the peak at 230 °C remains small, but it becomes clearly visible for catalysts with a higher Cu loading (catalyst D, 2.1 wt% Cu). If the exposure to the NO/O\(2\) mixture at 50 °C is omitted in these cases, only the peak around 230 °C disappears, while the peak around 130 °C is not affected.
The results shown in Figure 3 lead to several important conclusions:

1. The Cu-b species is a nitrogen-containing Cu$^{II}$ species. This is based on the observation that the NO-TPR peak around 230 °C is only observed after oxidation of the catalyst in the NO/O$_2$ mixture, while it is not present after oxidation in O$_2$ only.

2. The formation of the Cu-b species is enhanced when the NO/O$_2$ mixture reacts with the reduced Cu$^I$ species, probably Cu(NH$_3$)$_2^+$. This species is formed by reduction in NO/NH$_3$ at 200 °C. Exposure of oxidized Cu to the NO/O$_2$ mixture at 50 °C results in a significantly smaller NO-TPR peak around 230 °C, indicating a smaller amount of the Cu-b species.

3. The Cu-a species is a Cu$^{II}$ species that does not contain nitrogen, since it is present after oxidation in O$_2$ at 500 °C, and does not require exposure to the NO/O$_2$ mixture. This result also indicates that the Cu-a species does not react with NO alone. The most obvious candidates for the Cu-a species are Cu$^{II}$-oxide or hydroxide species.

We have now established that the Cu-b species corresponds to a nitrogen-containing Cu$^{II}$ species. A quantitative analysis of the NO-TPR peak at 230 °C indicates that the nitrogen-containing Cu$^{II}$ species is a Cu(NO$_3$)$_2$, as follows. By integration of the NO-TPR data shown in Figure 2, the total consumption of NO in the reduction is determined, and compared with the Cu content in the
catalysts, to obtain the number of NO molecules consumed per Cu atom. Table 2 summarizes these results for the catalysts A-F. We see that the number of consumed NO molecules per Cu atom equals 3 for the catalysts with a higher Cu content (D, E, and F). For the catalysts with a lower Cu-content, the NO/Cu ratio becomes lower. It is noted that precisely the catalysts where the Cu-α species is found, are also the catalysts exhibiting NO/Cu ratios lower than 3. A graph of these data is given in Figure 4, showing that the catalysts D, E, and F fall on the dashed line, which indicates the stoichiometric NO/Cu ratio of 3.

Table 2 - Total NO consumption (mmol/g) in NO-TPR of Cu-CHA catalysts and NO/Cu ratio, after exposure of oxidized Cu-CHA catalysts to a mixture of 800 ppm NO and 900 ppm NH₃.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu content (dry matter basis)</th>
<th>Total NO consumption TPR</th>
<th>NO/Cu ratio</th>
<th>NO consumption 120 °C (Cu-α)</th>
<th>NO consumption 230 °C (Cu-β)</th>
<th>Total CuII*</th>
<th>NOx conversion (200 °C)</th>
<th>SCR rate constant (200 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.126</td>
<td>0.129</td>
<td>1.02</td>
<td>0.07</td>
<td>0.059</td>
<td>0.090</td>
<td>0.039</td>
<td>0.92</td>
</tr>
<tr>
<td>B</td>
<td>0.214</td>
<td>0.446</td>
<td>2.08</td>
<td>0.13</td>
<td>0.316</td>
<td>0.235</td>
<td>0.104</td>
<td>2.78</td>
</tr>
<tr>
<td>C</td>
<td>0.287</td>
<td>0.602</td>
<td>2.10</td>
<td>0.11</td>
<td>0.492</td>
<td>0.274</td>
<td>0.194</td>
<td>4.91</td>
</tr>
<tr>
<td>D</td>
<td>0.33</td>
<td>0.990</td>
<td>3.00</td>
<td>0.03</td>
<td>0.96</td>
<td>0.350</td>
<td>0.230</td>
<td>5.98</td>
</tr>
<tr>
<td>E</td>
<td>0.451</td>
<td>1.359</td>
<td>3.01</td>
<td>0</td>
<td>1.359</td>
<td>0.453</td>
<td>0.294</td>
<td>8.40</td>
</tr>
<tr>
<td>F</td>
<td>0.547</td>
<td>1.630</td>
<td>2.98</td>
<td>0</td>
<td>1.63</td>
<td>0.543</td>
<td>0.316</td>
<td>9.33</td>
</tr>
</tbody>
</table>

* The total amount of CuII is calculated as the sum of the NO consumption at 120 °C and 1/3 of the consumption at 230 °C.

Figure 4 - Total consumption of NO in NO-TPR as a function of the Cu content in Cu-CHA catalysts, after exposure of the reduced state of the Cu-CHA catalysts to a mixture of 800 ppm NO and 900 ppm NH₃. The dashed line corresponds to the stoichiometric ratio NO/Cu of 3.
The stoichiometric NO/Cu ratio of 3 points to the reduction of Cu(NO₃). In an earlier publication, we presented a reaction cycle for NH₃-SCR, in which a Cu(NO₃) species reacts with NO to form a Cu-NO₂ species and an NO₂ (g) molecule, followed by further reduction with NH₃ and NO to Cu⁺ [9]. According to that reaction cycle, the net reaction for the reduction of the Z-Cu-(NO₃) can be written as:

\[
Z - Cu^{2+} - (NO_3)^- + 3 NO + 4 NH_3 \rightarrow 4 N_2 (g) + 6 H_2O (g) + Z - Cu^+
\]  
(3)

If we take the formation of the Cu(NH₃)₂⁺ complex into account, then Eq. (3) is modified to:

\[
Z - Cu^{2+} - (NO_3)^- + 3 NO + 6 NH_3 \rightarrow 4 N_2 (g) + 6 H_2O (g) + Z - Cu(NH_3)_2^+
\]  
(4)

Both equations show that the reduction of a Z-Cu-(NO₃) species in a mixture of NO and NH₃ requires 3 NO molecules per Cu atom. Therefore, the observed consumption of 3 NO molecules per Cu atom indicates that, for the catalysts with a Cu load above 2 wt% (catalysts D,E,F), all Cu is present as Cu(NO₃) species in the NO-TPR measurement. The NO-TPR profile for these catalysts show only the presence of the Cu-b species, which therefore can be assigned to a Cu(NO₃) species.

The assignment of the Cu-b to Cu(NO₃) is supported by FTIR results for similar Cu-CHA catalysts “CHA15_05” and “CHA15_02” in [16], where a Cu(NO₃) phase is detected after an identical pretreatment. XAS and EPR measurements also indicate that a Cu(NO₃) species is formed in reactions of the Cu(NH₃)₂⁺ complex with mixtures of NO and O₂ [9]. Furthermore, the NO consumption in a NH₃+NO temperature-programmed selective reduction measurement on a Cu-CHA catalyst with adsorbed nitrates, which is essentially the same as the NO-TPR measurements presented here, shows a consumption of NO that is quite similar to the curves presented here, especially when the nitrate phase is formed at 120 °C [17].

The catalysts with a lower Cu content (catalysts A, B, and C) show the presence of the Cu-a species in the NO-TPR profiles (see Figures 2 and 3), which we assign to a Cu²⁺-oxide or hydroxide species. This means that for Cu-CHA catalysts with a lower Cu-loading, not all Cu atoms form a stable Cu(NO₃) species. Since this peak does not correspond to a Cu(NO₃) species, the stoichiometric ratio NO/Cu becomes lower than 3. Starting from a CuO species, which is half of a Cu-O₂-Cu dimeric species, the reduction to Cu(NH₃)₂⁺ in an NO/NH₃ mixture can be written as follows:

\[
CuO + 2 NO + 4 NH_3 \rightarrow Cu(NH_3)_2^+ + 2 N_2 + 3 H_2O
\]  
(5)

The reduction of a Cu-OH species, to Cu(NH₃)₂⁺ in the NO/NH₃ mixture follows the reaction [6,9,31]:

\[
Cu - OH + NO + 3 NH_3 \rightarrow Cu(NH_3)_2^+ + N_2 + 2 H_2O
\]
This means that the stoichiometric ratio NO/Cu for the reduction of the Cu-\(a\) species is expected to be between 1 and 2, dependent on the type of Cu-oxide species in the catalyst. In any case, this stoichiometric value lower than 3, is in full agreement with the experimental result (Table 2). Assuming a stoichiometric factor of 1 for the Cu-\(a\) species, the total amount of Cu\(^{III}\) species (see Table 2) matches the Cu content as measured with ICP for all catalysts, except for catalyst A. For catalyst A, the total amount of Cu\(^{III}\) from NO-TPR is lower, indicating that either not all Cu has been oxidized, or that there could be another Cu\(^{II}\) phase that is not reduced in the mixture of NH\(_3\) and NO up to 370 \(^\circ\)C.

To evaluate the catalytic activity of the catalysts A-F, we have measured the NO\(_x\) conversion in the temperature range 160-550 \(^\circ\)C; the results are shown in the left panel of Figure 5. The first order rate constant for the NH\(_3\)-SCR reaction at 200 \(^\circ\)C, calculated according to Eq. 1, is used as a measure for the activity. The values for the NO\(_x\) conversion and rate constants are also included in Table 2. The development of the rate constants with the total Cu content, as determined by ICP is shown by the red squares in Figure 5, right panel. These data follow the familiar pattern for Cu-CHA catalysts, with a disproportionately low activity for catalysts with low Cu loading [10,11]. This could mean that there exists a critical Cu loading for the low-temperature activity of Cu-CHA catalysts in the NH\(_3\)-SCR reaction. There are also indications that the NH\(_3\)-SCR activity at low Cu loadings actually is proportional to the square of the Cu-loading, which would also explain this pattern. The latter explanation has led to the conclusion that the NH\(_3\)-SCR reaction actually requires pairs of Cu ions, which are formed through diffusion of mobile Cu-(NH\(_3\))\(^{2+}\) complexes [10,11].

The NO-TPR results presented above show that the Cu-CHA catalysts with low Cu loading contain both Cu-\(a\) and Cu-\(b\) species, while catalysts with a high Cu-loading only have Cu-\(b\). Based on this result, it is suggested that only Cu-\(b\) contributes to the low-temperature activity, implying that only the Cu that is able form Cu(NO\(_3\)) contributes to the NH\(_3\)-SCR activity. This would explain the

\[\text{Figure 5} - \text{Left: Measured NO}_x\text{ conversion for catalysts A-F, (feed gas: 500 ppm NO, 533 ppm NH}_3\text{, 5\% H}_2\text{O, 10\% O}_2\text{, balance N}_2\text{; flow: 225 Nml/min, 5 mg catalyst). Right: NH}_3\text{-SCR activity expressed as 1}\text{^{st}}\text{ order rate constants at 200 }^\circ\text{C as a function of the total Cu content (ICP, red) and the amount of Cu-b (Cu(NO}_3\text{)) from NO-TPR (blue).}\]
disproportionally low activity of the Cu-CHA catalysts with low Cu loading, since only a fraction of their total Cu loading would be active. To verify this hypothesis, we compare the activity of the Cu-CHA catalysts at 200 °C with respect to the total Cu content of the catalysts (ICP), and with respect to the amount of Cu-\(b\). Since it requires 3 NO molecules to reduce a single Cu(NO\(3\)) group, the amount of Cu-\(b\) is given by \(1/3\) of the NO consumption in the corresponding NO-TPR peaks, shown in Figure 2. The blue dots in the right panel in Figure 5 show this comparison of the NH\(_3\)-SCR activity at 200 °C and the amount of Cu-\(b\) determined from the NO-TPR measurement. We see, that in the catalysts with low Cu loading, the activity becomes proportional to the amount of Cu-\(b\), supporting the hypothesis that only Cu-\(b\) contributes to the NH\(_3\)-SCR activity in these catalysts.

**NO-TPR on SO\(_2\)-exposed Cu-CHA**

The NO-TPR procedure used for the SO\(_2\) exposed and regenerated catalysts is different from those presented above. The first NO-TPR sequence was similar to the procedure shown in Figure 1, except that the reduction step, in the pretreatment, at 200 °C in NO+NH\(_3\) was omitted, which implies that the Cu-nitrate phase is formed by reaction of NO + O\(_2\) at 50 °C with oxidized Cu. The heating ramp during the NO-TPR measurement ended at 270 °C, and the catalyst is then left in the reduced state. The end temperature of 270 °C was chosen to avoid any unwanted regeneration of the SO\(_2\) exposed catalysts. In the second NO-TPR sequence, the reduced catalyst was cooled in 10% O\(_2\), first to 150 °C where it was kept for 1 h, and then further to 50 °C; this procedure leaves the catalyst in the reduced state. From this point on, the sequence is similar to that shown in Figure 1, with a Cu-nitrate formation step and in NO/O\(_2\) followed by the NO-TPR in NO+NH\(_3\).

![Figure 6 - Schematic illustration of the NO-TPR procedure used on the sulfated and regenerated catalysts, showing the temperature profile (black line) and the employed gas mixtures (white and grey areas). The total flow rate was always 200 Nml/min with N\(_2\) as carrier gas.](image-url)
An additional change in the NO-TPR procedure was made for the sulfated catalysts due to the thermal stability of the Cu,S species. Therefore, in order to preserve the Cu,S species in the SO\textsubscript{2} exposed catalysts, the initial activation in O\textsubscript{2} was lowered to 150 °C. Since the regenerated catalysts had already been exposed to 550 °C for several hours, the activation at 500 °C was assumed to not to affect the state of the Cu,S species in these catalyst samples.

Since the activity of the Cu-CHA catalysts is related to the NO consumption after exposing the reduced state of the catalyst to the NO/O\textsubscript{2} mixture, only the second NO-TPR measurement of the fresh, SO\textsubscript{2} exposed and regenerated catalysts is considered here, since this procedure is related to Cu-nitrate formation on reduced Cu. The results are summarized in Figure 7. Qualitatively, the trend for both the SO\textsubscript{2} exposed and regenerated catalysts is that the NO consumption peaks becomes smaller with increasing SO\textsubscript{2} exposure time. Table 3 summarizes the total NO consumption found by integration of the NO-TPR peaks, and the relation of the total NO consumption to the Cu content, S content, and measured deactivation.

![Figure 7 - NO consumption curves for the second NO-TPR sequence of the fresh (black dashed lines), SO\textsubscript{2} exposed (red lines), and regenerated (blue lines) catalysts as functions of the temperature.](image)

The NO consumption in the fresh catalyst corresponds to an active Cu loading of 0.359 mmol/g\textsubscript{cat}, calculated as 1/3 of the NO consumption. This loading of active Cu in the fresh catalyst accounts for 73% of the total Cu loading measured with ICP (0.494 mmol/g\textsubscript{cat}).
The amount of active Cu determined from NO-TPR, Cu_{NO-TPR} loading, in the SO_2 exposed catalysts are in the range 0.109-0.227 mmol/g_{cat}, which overlaps with that of the low Cu loading samples A-C. With this in mind, it is interesting to note that the NO consumption around 130 °C (Cu-\textit{a} species) is not present in the sulfated catalysts (see Figures 2 and 7). This can only be a consequence of the sulfur preventing reduction of the Cu-\textit{a} species.

**Table 3 - NO consumption, Cu loading from NO-TPR, S content from ICP and deactivation from SCR activity measurements.** The Cu loading for the fresh catalyst as determined by ICP is 0.494 mmol/g_{cat}.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO consumption</th>
<th>Cu_{NO-TPR}</th>
<th>S/Cu</th>
<th>S/Cu_{NO-TPR}</th>
<th>Cu_{NO-TPR} - S</th>
<th>Deactivation @220 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>1.077</td>
<td>0.359</td>
<td>0</td>
<td>0</td>
<td>0.359</td>
<td>0</td>
</tr>
<tr>
<td>Sulf(1h)</td>
<td>0.682</td>
<td>0.227</td>
<td>0.37</td>
<td>0.51</td>
<td>0.177</td>
<td>0.73</td>
</tr>
<tr>
<td>Sulf(5h)</td>
<td>0.598</td>
<td>0.200</td>
<td>0.56</td>
<td>0.77</td>
<td>0.084</td>
<td>0.79</td>
</tr>
<tr>
<td>Sulf(15h)</td>
<td>0.351</td>
<td>0.117</td>
<td>0.94</td>
<td>1.30</td>
<td>-0.107</td>
<td>0.94</td>
</tr>
<tr>
<td>Sulf(65)</td>
<td>0.326</td>
<td>0.109</td>
<td>1.02</td>
<td>1.40</td>
<td>-0.145</td>
<td>0.96</td>
</tr>
<tr>
<td>Regen(1h)</td>
<td>0.929</td>
<td>0.310</td>
<td>0.09</td>
<td>0.13</td>
<td>0.313</td>
<td>0.12</td>
</tr>
<tr>
<td>Regen(5h)</td>
<td>0.924</td>
<td>0.308</td>
<td>0.11</td>
<td>0.14</td>
<td>0.307</td>
<td>0.19</td>
</tr>
<tr>
<td>Regen(15h)</td>
<td>0.874</td>
<td>0.291</td>
<td>0.14</td>
<td>0.20</td>
<td>0.287</td>
<td>0.19</td>
</tr>
<tr>
<td>Regen(65h)</td>
<td>0.840</td>
<td>0.280</td>
<td>0.16</td>
<td>0.22</td>
<td>0.281</td>
<td>0.21</td>
</tr>
</tbody>
</table>

In the SO_2 exposed and regenerated catalysts, the Cu content does not change, but the uptake of sulfur causes changes to the activity. In Chapters 2-6 it was concluded that the sulfur is associated with the Cu, but so far, it has only been possible to relate the uptake of sulfur to the total Cu content because there was no method available to measure the amount of active Cu. This is now possible with the NO-TPR method.

Under the assumption that a single sulfur species occupies a single Cu site, the remaining active Cu in the SO_2 exposed and regenerated catalysts can be determined in two ways. It can be calculated by subtracting the sulfur content (ICP) from the total active Cu content determined with NO-TPR on the fresh catalyst (Cu_{NO-TPR,Fresh} - S_{ICP}), or it can be measured directly with NO-TPR (Cu_{NO-TPR,Sulf/Regen}). In Figure 8, these two ways of determining the remaining active Cu are compared for the SO_2 exposed and regenerated catalysts by plotting the calculated remaining active Cu against the measured. The grey dashed line is the 1:1 correlation; above this line the amount of measured active Cu is less than anticipated from the sulfur content, and below the measured amount is larger than the calculated. For the regenerated catalysts, the correlation between calculated and measured active Cu falls nicely on the 1:1 line. This suggests that it is possible to measure active Cu in regenerated Cu-CHA catalysts, and corroborates that the deactivation in these catalysts occur via a single site-blocking mechanism.

The SO_2 exposed catalysts are below the 1:1 correlation, indicating that there is more active Cu than expected from the sulfur content measured with ICP. Recalling that the deactivation of the
SO\textsubscript{2} exposed catalysts was disproportionately larger than the S/Cu ratio, it would be expected that the measured active Cu would be less than the calculated, or on the 1:1 line. This indicates that sulfur is not associated with Cu, or that sulfur has been released during the pretreatment. The latter option is consistent with observations of SO\textsubscript{2} desorption around 270 °C during the first NO-TPR sequence. Consistently, such SO\textsubscript{2} desorption was not observed for the regenerated catalysts. The quality of the data was not sufficient for quantification, but qualitatively the SO\textsubscript{2} desorption was largest from the SO\textsubscript{2} exposed catalysts with the longest exposure times. This is consistent with the larger deviation from the 1:1 line of the Sulf(15h) and Sulf(65h) catalysts than the Sulf(1h) and Sulf(5h) catalysts.

Figure 8 - The calculated active Cu loading assuming 1 S deactivates 1 active Cu, Cu\textsubscript{NO-TPR,Fresh} - S\textsubscript{ICP}, plotted as function of the active Cu loading of the SO\textsubscript{2} exposed (black squares) and regenerated (red dots) catalysts measured with NO-TPR, Cu\textsubscript{NO-TPR,Sulf/Regen}. The grey dashed line is the 1:1 proportionality line.

For the regenerated catalysts, the deactivation measured in Chapter 5 was slightly higher than the corresponding S/Cu\textsubscript{ICP} ratios, which is shown by the black squares in Figure 9. The NO-TPR measurement on the fresh catalyst indicated that only 73% of the total Cu loading was active, which may be the reason for the slight offset of the S/Cu\textsubscript{ICP} from the 1:1 proportionality. Therefore, the S/Cu\textsubscript{ICP} was corrected for active Cu by dividing by 0.73 to obtain the S/Cu\textsubscript{NO-TPR}, which are the red dots in Figure 9. As seen, this leads to a better 1:1 correlation between the deactivation and the S/Cu ratio. This emphasizes the applicability of the NO-TPR method for regenerated Cu-CHA catalysts, and the importance of relating sulfur to the active Cu content.
Discussion

The NO-TPR results clearly indicates the presence of two types of Cu in Cu-CHA catalysts, that are distinguished by the reaction product of the oxidation of Cu$^{+}$ (Cu(NH$_3$)$_2^+$) with a mixture of NO and O$_2$. One type of Cu, Cu-$b$, forms a Cu(NO$_3$) species, and the other type, Cu-$a$, forms a Cu-oxide or Cu-OH species. If the Cu content is sufficiently high, all Cu in a Cu-CHA catalyst is Cu-$b$, while in catalysts with a lower Cu content, some Cu-$a$ is present as well. The NH$_3$-SCR activity appears to be related to the ability of the Cu-CHA catalyst to form the Cu(NO$_3$) phase. Since the formation of Cu(NO$_3$) is enhanced on a reduced Cu-CHA (Figure 3, catalyst B, red curves) containing Cu(NH$_3$)$_2^+$, it is important that the amount of Cu(NO$_3$) is measured starting from Cu reduced in NO+NH$_3$.

The reason for the relation between Cu-$b$ and the NH$_3$-SCR activity is that the formation of Cu(NO$_3$) from Cu$^+$ or Cu(NH$_3$)$_2^+$ is part of the NH$_3$-SCR reaction cycle. In both the formation of Cu(NO$_3$) and the NH$_3$-SCR reaction, the dissociation of O$_2$ on the Cu$^+$ or Cu(NH$_3$)$_2^+$ species is an essential step. Dissociation of O$_2$ on Cu-CHA requires a reduced Cu species, and therefore, the enhanced formation of Cu(NO$_3$) on reduced Cu shown in Figure 3 is due to a more efficient activation of O$_2$. This enhanced formation of Cu(NO$_3$) on reduced Cu-CHA provides additional evidence for the explanation, that the much higher rate of NH$_3$-SCR, compared to the oxidation of NO to NO$_2$ on Cu-CHA catalysts, is due to the influence of the oxidation state of the Cu on the dissociation of the O$_2$. In NH$_3$-SCR, the dissociation of O$_2$ takes place on a Cu$^+$, and it is therefore much more efficient than in NO-oxidation. In NO-oxidation, much less Cu$^+$, if any, is available, or the dissociation of O$_2$ takes place on a Cu$^{II}$ phase, and is therefore slower.
The data in Table 2 show that the total amounts of Cu$^{II}$ determined from NO-TPR, assuming a stoichiometric factor NO/Cu-$a$ of 1 and NO/Cu-$b$ of 3, matches the amounts of Cu found from ICP, suggesting that all Cu is oxidized in the NO-TPR measurements. Recently, it has been shown that in the oxidation of the Cu$^I$ species in oxygen, some of the Cu$^I$ phase persists, while oxidation in NO$_2$ leads to a complete oxidation of the Cu$^I$ species [10]. Based on this, the conclusion that all Cu has been oxidized in the NO-TPR measurements is probably related to the presence of some NO$_2$ during the oxidation in the O$_2$/NO mixture (see Figure 1). This means that at least a part of the Cu$^{II}$ phase in the NO-TPR experiments is formed by a direct reaction between Cu$^I$ and NO$_2$. This means that the oxidic Cu-$a$ species in NO-TPR also can be the result of a decomposition of a Cu-(N,O) species, which implies that some Cu in the Cu-CHA catalysts does not form stable Cu(NO$_3$)$_2$ or other Cu-(N,O) species. For oxidic Cu species formed by decomposition of Cu-(N,O) species, it can be expected that they do not react with the NO/O$_2$ mixture, in line with our conclusion for the Cu-$a$ species in the NO-TPR measurements. An exception is catalyst A, in which there can be a larger contribution of a CuO phase, according to Eq. (4), or some reduced Cu may be present during the NO-TPR measurement, since there is a difference between the amount of Cu$^{II}$ in NO-TPR and the total amount of Cu found by ICP.

Measurements with EPR also indicate that, at least at low Cu loadings, a part of the visible Cu species are not affected by exposure to NO and O$_2$, also indicating that not all Cu in Cu-CHA catalysts is able to form stable Cu(NO$_3$)$_2$ [32]. The fact that such a Cu species is observed in EPR also means that it is a Cu$^{2+}$ species, since Cu$^+$ species are EPR silent. This matches the assignment of the Cu-$a$ species well: it must be a Cu$^{2+}$ species, because NO-TPR shows that it can be reduced in the NO/NH$_3$ mixture, but it is not affected by the exposure to the NO/O$_2$ mixture. Furthermore, the Cu-$a$ species is only observed for the Cu-CHA catalysts with a low Cu content. Therefore, the Cu-$a$ species observed in NO-TPR can very well be the same Cu species that does not form a Cu(NO$_3$)$_2$ species in EPR.

The dependence of the NH$_3$-SCR activity at 200 °C on the Cu density, as also shown by the red dots in Figure 5, is divided in two ranges. At high Cu loadings, the activity depends linearly on the total Cu loading. This agrees well with the interpretation of the NO-TPR data, that only the Cu-$b$ species contributes to the NH$_3$-SCR activity, since the amount of Cu(NO$_3$)$_2$ formed just corresponds to the Cu-content at higher Cu loadings. At low Cu-loadings, the NH$_3$-SCR activity becomes disproportionally low, and the data indicate that a critical amount of about 0.1 mmol/g Cu is needed to obtain activity at 200 °C. For low Cu loadings, it has been argued that there is a 2nd order dependence of the NH$_3$-SCR activity on the Cu loading, which indicates that the NH$_3$-SCR rate involves the formation of Cu-pairs. The distinction between a critical Cu loading and a 2nd order dependence cannot reliably be made, since it entirely depends on the measured amounts of Cu-$a$ and Cu-$b$ in a single data point (catalyst C). The NO-TPR data, however, clearly show that the NH$_3$-SCR activity becomes 0 when the amount of Cu-$b$ becomes 0, indicating that the ability to form a stable Cu(NO$_3$)$_2$ species is critical for the NH$_3$-SCR activity of Cu-CHA catalysts.

We note that the relative amount of the Cu-$a$ species becomes smaller, and that all Cu is present as a Cu-$b$ species at higher Cu loadings, probably with a slightly lower reduction temperature, as indicated by the widening of the NO-TPR peak at the low-temperature edge. This implies that it is possible to transform the inactive Cu-$a$ species to a Cu-$b$ species by increasing the Cu density.
This suggests that the formation of the Cu-b species follows from interaction of two Cu atoms. It is known that the dissociation of an oxygen molecule on a Cu-CHA catalyst becomes easier on a pair of Cu ions [10,18,20], and therefore, pairs of Cu ions are important intermediates for NH3-SCR. The fact that a Cu(NH3)2+ ion is mobile facilitates Cu pair formation, which gives rise to the high SCR activity of Cu-CHA at low temperatures. If we follow the idea that the activation of oxygen is the same for both Cu(NO3) formation and for NH3-SCR, then the amount of Cu(NO3) in NO-TPR should reflect the amount of Cu that can form Cu-pairs. Because formation of Cu-pairs depends on the mobility of the Cu(NH3)2+ complex [10], it can be expected that a certain fraction of the Cu is not able to form the Cu-nitrate species, and this fraction becomes smaller as the Cu-density increases. In NO-TPR, we find that the fraction of Cu that is able to form Cu(NO3) increases with Cu content (see Table 2), which is, at least qualitatively, in agreement with the scenario that Cu(NO3) formation also proceeds via O2 activation on Cu pairs.

The fact that a clear reduction is observed in NO-TPR after exposure of a reduced Cu to a mixture of NO and O2 at 50 °C (Figure 3), means that the oxidation of CuI already takes place at that temperature. The reduction associated with the Cu-b species, which determines the NH3-SCR activity, starts at around 150 °C, which is close to the light-off of the NH3-SCR reaction on Cu-CHA catalysts. This is not consistent with earlier conclusions that the dissociation of oxygen is the rate-limiting step for the NH3-SCR reaction. It seems that the unavoidable presence of NO2 in the mixture of NO and O2 is important here, and that NO2 facilitates the oxidation of CuI, in agreement with the observation that a complete oxidation of Cu is observed in the presence of NO2. A lower temperature for oxidation of CuI with NO2, compared to the reduction in NO/NH3, indicates that the NO2 indeed can enhance the rate of the NH3-SCR reaction to give the fast-SCR reaction, with a more rate-determining character for the reduction part of the NH3-SCR reaction [9].

An oxidation of CuI with NO2 would initially lead to a CuII-NO2- species, and the nitrate species is then formed in a second reaction step with NO2 to release an NO molecule, according to the known nitrite/nitrate equilibrium [17,27,33,34]:

\[
Cu - NO_2^- + NO_2 (g) \leftrightarrow Cu - NO_3^- + NO (g)
\]  

(7)

The NO-TPR data indicate that all Cu is present as a Cu(NO3) species at high Cu loadings, while at low Cu loadings, the nitrate is not stable on all Cu sites, as also indicated by previous EPR measurements [32]. Apparently, the Cu(NO3) species can be stabilized by increasing the Cu loading, suggesting that the formation of Cu pairs not only facilitates the dissociation of O2, but also plays a role in the stabilization of the Cu(NO3) species. Following the results presented in this chapter, the sites where this stabilization occurs are then also the active sites for NH3-SCR. The configurations of the Cu, where the Cu(NO3) species is not stable, cannot be derived from the NO-TPR measurements, but are most probably related to the way Cu is bound to the zeolite (e.g. Z-CuOH vs Z2-Cu), and the location of the Cu ions in the zeolite (6-ring or 8-ring).

**NO-TPR on SO2-exposed Cu-CHA**

The NO-TPR method applied here appeared to be fully applicable on the regenerated catalysts, which is probably due to the stable Cu,S species in these catalysts. This is not the case in the SO2 exposed catalysts, which is possibly due to the combination of the employed NO-TPR pretreatment
and the less stable Cu,S species in SO$_2$ exposed catalysts. To accommodate this in the NO-TPR method on the SO$_2$ exposed catalysts, the O$_2$ activation at 500 °C was avoided and the NO-TPR measurement was stopped at 270 °C instead of 370 °C. However, some SO$_2$ desorption was still observed around 270 °C during the first NO-TPR sequence, indicating some unintended loss of sulfur. In Figure 2B (Chapter 3) it can be seen that the SCR activity of an SO$_2$ exposed catalyst is unaffected by exposure up 300 °C in SCR gas, and in Figure 5A (Chapter 3) the SO$_2$ desorption from SO$_2$ exposed Cu-CHA monolith catalysts in a typical SCR reaction gas mixture starts around 270 °C. Furthermore, it has been suggested that the desorption of SO$_2$ from SO$_2$ exposed Cu-CHA catalysts is enhanced under more reducing conditions [32], which are closer to the conditions used in the actual NO-TPR measurement. Therefore, it is plausible that the unexpected results of the NO-TPR measurements on the SO$_2$ exposed catalysts is due to SO$_2$ desorption during the first NO-TPR sequence. It may be possible to avoid this by carrying out the reduction step at 200 °C, as presented in the general NO-TPR method, but a further development of the NO-TPR method is needed to resolve this.

**Conclusions**

We have introduced temperature programmed reduction with NO (NO-TPR) as a method to obtain direct and quantitative information about the reduction of Cu$^{II}$ species as it takes place in the NH$_3$-SCR reaction. In NO-TPR a mixture of NO and NH$_3$ is used to reduce the Cu$^{II}$ species, and the consumption of NO is measured as a function of the temperature. Since this procedure reflects the reduction part of the NH$_3$-SCR reaction, the observed reduction profiles are a direct reflection of the relevant reduction properties of Cu for NH$_3$-SCR.

The NO-TPR procedure consists of three phases, namely (1) the preparation of the Cu$^{II}$ phase, (2) exposure of the Cu$^{II}$ phase to a mixture of NO and NH$_3$ at the start temperature for the TPR procedure, and (3) the reduction of the Cu$^{II}$ phase in the mixture of NO and NH$_3$ during controlled heating. The results of the NO-TPR measurement depend on the way the Cu$^{II}$ phase is prepared. The most relevant results for the NH$_3$-SCR reaction were obtained by first preparing a Cu$^{I}$ phase in a mixture of 800 ppm NO and 900 ppm NH$_3$ followed by oxidation at 50 °C in a mixture of 2000 ppm NO in 10% O$_2$/N$_2$.

The NO-TPR results for series of Cu-CHA catalysts for NH$_3$-SCR, with different Cu loadings, ranging from 0.7 to 3.0 wt%, on the same parent material (Si/Al = 15), show a distinction between catalysts with a low and high Cu loading. At high Cu loadings, the NO consumption in the NO-TPR takes place between 150 and 250 °C, in a single broad peak with a maximum consumption at around 230 °C. In these cases, the total NO consumption corresponds to exactly 3 times the Cu content in the catalysts, which indicate that all Cu in the catalyst is present as a Cu(NO$_3$) species. At lower Cu-loadings the reduction occurs in two stages, with a reduction peak around 130 °C, and the Cu(NO$_3$) species around 230 °C, as also observed at higher Cu loadings. The reduction around 130 °C is due to the formation of a Cu$^{II}$-oxide or Cu$^{II}$-hydroxide phase in the zeolite. This means that for at low Cu loadings, not all Cu forms a stable Cu(NO$_3$) phase at 50 °C.

The low-temperature activity of the Cu-CHA catalysts is related to the amount of stable Cu(NO$_3$) that is observed in the NO-TPR measurement. For Cu-CHA with a low Cu-loading, this means that a certain fraction of the Cu does not contribute to the low-temperature NH$_3$-SCR activity; at
higher Cu loadings, all Cu contributes to the NH$_3$-SCR activity. The Cu(NO$_3$) phase is apparently stabilized at higher Cu loadings, indicating that Cu-Cu interactions play a role in the formation of the stable Cu(NO$_3$) phase.

The applicability of the NO-TPR method was also tested on SO$_2$ exposed and regenerated Cu-CHA catalysts. For the regenerated catalysts, the method appeared to be directly applicable, and lead to an improved relation between sulfur content and deactivation. For the sulfated catalysts, the NO-TPR method should be changed to accommodate the loss of sulfur from less stable Cu,S species.

References


Chapter 7

doi:10.1021/cs501673g.


Chapter 8

Summary, conclusions and future perspectives
Summary and Conclusions

The important task of efficiently removing NO\textsubscript{x} from diesel exhaust of heavy-duty vehicles is improved by the use of Cu-CHA NH\textsubscript{3}-SCR catalysts. However, the presence of SO\textsubscript{2} in diesel exhaust significantly deactivates Cu-CHA catalysts, and thereby diminish their ability to remove NO\textsubscript{x}. With the motivation of developing robust Cu-CHA catalysts to ensure the efficient removal of NO\textsubscript{x}, a solid fundamental understanding of the deactivation behavior of Cu-CHA catalysts by SO\textsubscript{2} was obtained. Supported by this fundamental understanding, it was concluded that the impact of SO\textsubscript{2} over the lifetime of the catalyst is not prohibitive for practical application. The anchor of the investigations was the assessment of the impact of different SO\textsubscript{2} treatments on the performance of the catalysts in the NH\textsubscript{3}-SCR reaction, further supported by several characterization techniques.

As Cu-CHA catalysts are exposed to SO\textsubscript{2}, particularly the low-temperature SCR activity of the catalysts is affected. It has been established that the deactivation of Cu-CHA catalysts by SO\textsubscript{2} is a consequence of chemical interactions between SO\textsubscript{2} and Cu sites, leading to formation of various Cu,S species. Consistently, the S/Cu ratios after exposure of Cu-CHA catalysts to SO\textsubscript{2} or mixtures of SO\textsubscript{2} and SO\textsubscript{3}, never exceeds 1 in any of the experiments conducted during this PhD work. This indicates that SO\textsubscript{2} selectively interacts with Cu sites in the catalysts, and precipitation of ammonium sulfate is not considered responsible for the deactivation of Cu-CHA catalysts by SO\textsubscript{2}. The direct Cu,S interactions also mean that the chemical composition of the zeolite framework (H\textsubscript{n}Al\textsubscript{n}Si\textsubscript{1-n}O\textsubscript{2} vs H\textsubscript{n}Si\textsubscript{n}AlP\textsubscript{1-n}O\textsubscript{4}), has little impact on the deactivation behavior.

The affinity of SO\textsubscript{2} for Cu depends on the oxidation state of Cu. SO\textsubscript{2} adsorbs more stably on Cu\textsuperscript{I} than on Cu\textsuperscript{II}, while SO\textsubscript{3} has a higher affinity for Cu\textsuperscript{II} than for Cu\textsuperscript{I}. In the relevant temperature interval for SCR in heavy-duty vehicles (180-550 °C), SO\textsubscript{3} is formed via oxidation of SO\textsubscript{2}. The rate of the oxidation increases with temperature to such an extent that the effect of admitting SO\textsubscript{3} together with SO\textsubscript{2} is only measurable at lower temperatures. Furthermore, since the presence of NO and NH\textsubscript{3} determines the oxidation state of the Cu, the effect of SO\textsubscript{3} and the formation of Cu,S species also depend on the reaction conditions.

In Cu-CHA catalysts, the main Cu\textsuperscript{II} sites are Z-CuOH and Z\textsubscript{2}-Cu, which are Cu charge-balancing one or two framework Al atoms, respectively. SO\textsubscript{2} and SO\textsubscript{3} mainly interacts with the Z-CuOH sites, while certain Z\textsubscript{2}-Cu sites are unaffected by SO\textsubscript{x}. The SO\textsubscript{2} resistant Z\textsubscript{2}-Cu sites are conceivably the reason why a 100% deactivation of the low-temperature activity has not been observed.

During exposure to SO\textsubscript{2} concentrations as low as 1.5 ppmv, Cu,S species are primarily formed on the Z-CuOH sites. The majority of the formed Cu,S species are unstable at 550 °C, and these Cu,S species are denoted reversible. Heating to 550 °C in SO\textsubscript{2}-free gas for minimum 4 h liberates the Z-CuOH sites fully from the reversible Cu,S species. The decomposition of the reversible Cu,S species begins close to 300 °C.

In parallel to the formation of the reversible Cu,S species, a more thermally stable Cu sulfate (denoted irreversible) is also formed, which has a decomposition temperature around 650 °C.
Hence, a full restoration of the low-temperature activity can be achieved by heating to 700 °C. Formation of the irreversible Cu sulfate appears to occur via a kinetically limited reaction that is enhanced by the presence of H$_2$O. The formation involves a relocation of sulfur from Z-CuOH sites to certain Z$_2$-Cu sites, and chemical changes to the Cu,S species on Z-CuOH sites. The irreversible Cu sulfate is only formed on a restricted fraction of the total Cu content.

Both the reversible and irreversible Cu,S species are suggested to deactivate Cu-CHA catalysts by a single site-blocking mechanism. However, the reversible and irreversible Cu,S species have significantly different impacts on the low-temperature SCR activity of Cu-CHA catalysts. Comparing the deactivation with the amount of Cu,S species in the catalyst, the reversible Cu,S species induces a disproportionately large deactivation for a single site-blocking mechanism. In contrast, the irreversible Cu,S species causes a 1:1 correlation between the deactivation and S/Cu ratio. Furthermore, the reversible Cu,S species leads to a change in the apparent activation energy for NH$_3$-SCR, whereas the apparent activation energy is unaffected by the irreversible Cu,S species. These different impacts are explained by a more significant contribution of the Z-CuOH sites than the Z$_2$-Cu sites to Cu pair formation that is important for the low-temperature SCR activity of Cu-CHA catalysts.

The deactivation of Cu-CHA catalysts by SO$_2$, appears to depend on the total SO$_2$ exposure, which is calculated as the product of the SO$_2$ concentration and the exposure time. It implies that the formation rate of the deactivating Cu,S species has a similar dependence on the exposure conditions. This dependency can be exploited to estimate the development and impact of Cu,S species via accelerated SO$_2$ exposures with higher SO$_2$ concentrations. During SO$_2$ exposures similar to those expected within the full lifetime of a Cu-CHA catalyst in a heavy-duty vehicle aftertreatment system, the formation of reversible Cu,S species occurs fast. The formation rate has a volcano-like dependence on the exposure temperature. Within the range 200-500 °C, the fastest formation rates are at intermediate temperatures of 300-400 °C. Despite this influence of exposure temperature, S/Cu ratios 0.5 are reached for all exposure temperatures within the first 13% of the lifetime SO$_2$ exposure. Due to the disproportionately large impact of the reversible Cu,S species on the low-temperature activity, the deactivation builds up even faster than the reversible Cu,S species. Thus, deactivation levels of at least 80% for all exposure temperatures, are reached already within 5% of the lifetime SO$_2$ exposure. The formation of irreversible Cu sulfate is similarly fast, but restricted to a minor fraction of Cu. This is regardless of exposure time and independent of the exposure temperature, which is likely a consequence of the similar regeneration treatments at 550 °C that all catalyst samples were exposed to before measurement of the irreversible Cu sulfate amounts. The deactivation by the irreversible Cu sulfate is therefore, restricted to about 30% throughout the lifetime SO$_2$ exposure.

In terms of the applicability of Cu-CHA catalysts in exhaust aftertreatment systems of heavy-duty vehicles, the results presented in this thesis show that the significant impact of low concentrations of SO$_2$ on the low-temperature activity is a present issue. Therefore, Cu-CHA catalysts are best employed when diesel with low sulfur content, as in ultra-low sulfur diesel, is used as fuel. Despite the use of ultra-low sulfur diesel, deactivation occurs fast, and hence, application of Cu-CHA catalysts are contingent on effective regeneration strategies in order to maintain efficient use of the catalysts’ good low-temperature activity. The potential impact of SO$_3$ exposure, formed via
SO$_2$ oxidation on upstream aftertreatment components, appears only to be concern at low temperatures. However, under SCR conditions at low temperature, a significant fraction of Cu will be present as Cu$^+$ on which SO$_2$ adsorbs more stably, and therefore, the impact of SO$_3$ may also be of little importance at low temperatures.

Finally, temperature programmed reduction of NO (NO-TPR) has been developed as a new method to measure the active amount of Cu in Cu-CHA catalysts in NH$_3$-SCR. The NH$_3$-SCR activity depends on the ability of the Cu-CHA catalysts to form a stable Cu-nitrate species. Initial explorative tests of the NO-TPR method on SO$_2$ exposed Cu-CHA catalysts indicate that the irreversible deactivation that remains after regeneration at 550 °C, most likely caused by the formation of Cu sulfate, can be monitored by the NO-TPR method. For the SO$_2$ exposed samples, the method needs to be developed further, since the changes to the reversible Cu,S phases and the interactions with the ammonia and NO in the reduction are not well understood yet.

**Future perspectives**

The use of Cu-CHA catalysts for NH$_3$-SCR is especially promoted by their better activity in the low-temperature region for SCR in automotive aftertreatment systems, compared to other SCR catalysts. Maintaining the better low-temperature activity in the presence of SO$_2$ is contingent on efficient regeneration. In this work regeneration has typically been carried out for at least 4 h at 550 °C in SO$_2$-free gas, to achieve the maximum possible regeneration at 550 °C. However, these regeneration conditions are unrealistic in an actual aftertreatment system. Therefore, several topics within regeneration should be explored to establish how efficiently regeneration in aftertreatment systems can be carried out. The first topic, which may be the most important, is to identify the “critical” SO$_2$ concentration for regeneration. As shown in this thesis, even at 500 °C the deactivation builds up in the presence of 1.5 ppmv SO$_2$, but is lowered in SO$_2$-free gas. This means that somewhere in the SO$_2$ concentration range 0-1.5 ppmv, there is a critical concentration of SO$_2$ where regeneration occurs, which would be an important parameter for developing regeneration strategies. It is possible that this concentration is lower than what is practically achievable, and hence, other approaches for efficient regeneration should be explored. Furthermore, as engine operating temperatures are generally lowered, thermal regeneration may not be an option in the future. An alternative approach could be to increase the reduction properties of the exhaust gas, since there are indications that more reducing gas atmospheres promote the decomposition of deactivating Cu,S species. This could potentially be achieved by tuning the concentrations of O$_2$, CO or NH$_3$, but requires further investigations.

The results presented in this work strongly points to a certain influence of the coordination environment of Cu on the stability of the formed Cu,S species, and some Cu sites even appeared to be entirely inert to SO$_2$ exposure. Therefore, an increased understanding of how the zeolite structure, and the Al-distribution, affects the Cu,S interactions would be beneficial for developing and tailoring more SO$_2$ resistant Cu-zeolite catalysts. This may be realized either by controlling the locations of Al or by employing other zeolite structures.
Appendices
Appendix A
Appendix A

Supporting information to:

Reversible and irreversible deactivation of Cu-CHA NH$_3$-SCR catalysts by SO$_2$ and SO$_3$

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Monolith experiments - NO\textsubscript{x} conversion data and Arrhenius plots of fresh, sulfated and regenerated catalysts

Steady state NO\textsubscript{x} conversions were measured on 8 samples of the same Cu-CHA/cordierite monolith catalyst, which were exposed to 8 different SO\textsubscript{x} treatments. The measured NO\textsubscript{x} conversions of fresh, sulfated and regenerated states of the tested catalysts are shown as functions of temperature in Figure S1 and the corresponding data points are listed in Table S1 below.
Figure S1 – Steady state NO\textsubscript{x} conversions as functions of temperature for Cu-CHA catalysts in their fresh, sulfated and regenerated states. The SO\textsubscript{x} treatment conditions are displayed in each plot. The regeneration conditions were the same for all catalysts, i.e. heating to 550 °C for 4 h in SCR gas.
Table S1 – Data for measured NO\textsubscript{x} conversions of fresh, sulfated and regenerated states of the catalysts.

<table>
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<th>SO\textsubscript{x} treatment</th>
<th>Fresh</th>
<th>Sulfated</th>
<th>Regenerated</th>
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<td>Temperature [°C]</td>
<td>NO\textsubscript{x} conversion</td>
<td>Temperature [°C]</td>
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<tr>
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<td>170</td>
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<td>SO\textsubscript{3}-550</td>
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Based on the measured steady state NO\textsubscript{x} conversions of the tested catalysts, rate constants were calculated in order to make Arrhenius plots. For the elaboration of the Arrhenius plots, the rate constants for NO\textsubscript{x} conversions below 70 % for the fresh and regenerated states of each of the catalysts, were first combined to determine a common slope. Thereafter, the intersect was determined individually for the fresh and regenerated states of the catalysts with fixed slopes. The slopes and intersects of the sulfated states of the catalysts were determined simultaneously. The resulting Arrhenius plots for the fresh, sulfated and regenerated states of the tested catalysts are shown in Figure S2.
Figure S2 – Arrhenius plots of fresh, sulfated and regenerated states of al tested catalysts.
Appendix A

Desorption of SO\textsubscript{2} – detailed SO\textsubscript{2} desorption plots

During heating for regeneration at 550 °C in SCR gas and during heating to 900 °C in N\textsubscript{2}, SO\textsubscript{2} desorbed from the catalysts, and the outlet concentration of SO\textsubscript{2} was measured, which is plotted in Figure S3 and Figure S4.

Figure S3 – SO\textsubscript{2} desorption from SO\textsubscript{x} exposed catalysts during heating to 550 °C for regeneration in SCR gas.

Figure S4 – SO\textsubscript{2} desorption from regenerated catalysts during heating to 900 °C in N\textsubscript{2}. 
Discussion – calculations for determination of the internal effectiveness factor

In order to assess if internal diffusion limitations can be responsible for the drop in activity that is observed after exposure to SO$_2$, the internal effectiveness factor, $\eta$, is calculated. For a first order reaction in a spherical crystal the internal effectiveness factor can be expressed as a function of the Thiele modulus, $\phi$, as shown in Eq. (S1) [1].

$$\eta = \frac{3}{\phi^2} \left( \frac{\phi}{\tanh(\phi)} - 1 \right)$$  \hspace{1cm} (S1)

For a first order reaction, the Thiele modulus can be expressed by a relation between the crystal radius, $R$, the intrinsic volume based rate constant, $k_V$, and the effective diffusion coefficient, $D_{eff}$, which is shown in Eq. (S2) [1]. The volume based rate constant is obtained by multiplying the catalyst weight based rate constant by $22.4 \cdot 10^{-3}$ m$^3$/mol and by the density of the catalyst, $\rho_{cat} = 1544 \cdot 10^3$ g/m$^3$, which has been calculated based on the CHA framework density and the Cu-loading of the catalyst.

$$\phi = R \sqrt{\frac{k_V}{D_{eff}}} = R \sqrt{\frac{k \cdot 22.4 \frac{L}{mol} \cdot \rho_{cat}}{D_{eff}}}$$  \hspace{1cm} (S2)

The crystal radius is approximately $0.5 \cdot 10^{-6}$ m, as verified with scanning electron microscopy. The rate constant at 183 °C for the fresh state of the catalyst before exposure to SO$_2$ at 200 °C with H$_2$O present is used in the calculations for the intrinsic rate constant, which is $390$ s$^{-1}$. Effective diffusion coefficients of NH$_3$ in a Cu-CHA catalyst have been measured with quasielastic neutron scattering at 0, 50 and 100 °C [2]. Using the activation energy for the diffusion (4.4 kJ mol$^{-1}$) [2], extrapolation of the experimental diffusion coefficients to 180 °C has been done to obtain the value $1.2 \cdot 10^{-9}$ m$^2$ s$^{-1}$, for the effective diffusion coefficient used here to calculate the effectiveness factor for the fresh Cu-CHA catalyst.

References
Appendix A
Appendix B
List of publications


