Doctoral Thesis

High temperature desulfurization of biomass-derived synthesis gas probed by X-ray absorption spectroscopy

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High Temperature Desulfurization of Biomass-derived Synthesis Gas Probed by X-ray Absorption Spectroscopy

A dissertation submitted to
ETH ZURICH

for the degree of
Doctor of Sciences

presented by
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2013
“[...] und der uralte Zauber, daß der Besitz des richtigen Wortes Schutz vor der ungezähmten Wildheit der Dinge gewährt, erwies seine beruhigende Macht wie vor zehntausenden Jahren.

Robert Musil, Der Mann ohne Eigenschaften
Abstract of this thesis

Supply with sustainable energy and fuels is one major task of the 21st century. One such sustainable source for fuels and energy is biomass, which has been used as energy carrier by mankind from its beginning. A particularly attractive recent option is converting wood into synthetic natural gas (SNG), which is primarily composed of methane (CH$_4$). This process mainly consists of gasification of the wood, cleaning of the generated gas from impurities, and subsequent catalytic methane synthesis. After this wood-to-SNG process has proved its general feasibility, some hurdles for competitive market implementation remain. Among these hurdles is gas cleaning. Currently, gas cleaning is performed after high temperature gasification in low temperature processes, where tars, sulfur species and water are removed from the gas by liquid scrubbing. Sulfur removal is required to protect downstream catalysts from poisoning and equipment from corrosion. Before subsequent methanation at 300 - 400 °C, water needs to be evaporated for adjustment of the H$_2$ to CO ratio by means of the water-gas shift reaction. This causes not only thermal losses due to cooling and reheating, but also requires investment for heat exchangers and evaporators, ultimately increasing the overall costs of the wood-to-SNG process.

To overcome the inefficient low-temperature cleaning, several options for high-temperature gas cleaning from sulfur impurities are proposed, of which three will be discussed in this thesis. All processes have in common the concept of periodic sulfur uptake by a solid material and subsequent regeneration, allowing a separation of the sulfur from the gas stream. To understand these processes, time-resolved X-ray absorption spectroscopy (XAS) was employed to probe the transient solid phase, while simultaneous mass spectrometry was used to study the activity of the system by analysis of the gas phase. This allows proposing mechanisms for sulfur transport over the different materials, which in turn allow dedicated development and optimization of materials and processes for sulfur removal.

Manganese-based sorbents were studied for their ability to remove H$_2$S from a gas stream at high temperatures. It was shown that the sorbents remove H$_2$S from the gas over multiple cycles and release the sulfur as SO$_2$ under oxidizing conditions. A two-step mechanism for sulfidation of manganese was found, indicating that SO$_2$ is generated by reduction of Mn$_3$O$_4$ with H$_2$S. This undesired reaction impedes complete desulfurization under the tested conditions.
In a next step, the removal of H$_2$S and organic sulfur species by molybdenum catalysts was investigated. Here, thiophene (C$_4$H$_4$S) was used as model compound for organic sulfur species. It was found that the tested Mo/Al$_2$O$_3$ catalyst efficiently removes H$_2$S and C$_4$H$_4$S from the gas stream in the absence of steam over multiple cycles. The presence of steam decreased reactivity towards sulfur, which was shown to be due to competitive adsorption of H$_2$O to the surface of the Mo catalyst, preventing sulfur species from adsorbing.

Integration of sulfur removal and methanation was studied over Al$_2$O$_3$ supported ruthenium catalysts. Regeneration of the sulfur-poisoned catalyst and removal of sulfur from the feed was successfully tested over multiple cycles. The interaction of the Al$_2$O$_3$ support with sulfur was found to prevent efficient regeneration of the catalyst. After oxidation, sulfur is completely removed from Ru, but is stored on the support. Subsequent exposure to methanation conditions releases sulfur from the support, causing poisoning of the Ru catalyst.

In conclusion, mechanistic details of the three tested desulfurization processes could be clarified. This was largely supported by the improvement of the sensitivity of XAS. To increase the sensitivity, a modulated excitation scheme was employed, where the changes in the sample’s structure are enhanced by filtering of the XAS spectra. This methodological development matches well the requirements for studying transient desulfurization processes, but can be used for a much larger range of experimental studies. It is expected that the mechanistic insights that were obtained in this thesis will help making the production of SNG from wood more efficient.
Kurzfassung


Mangan-basierte Sorptionsmaterialien wurden auf ihre Fähigkeit hin untersucht, Schwefelwasser-
stoff \((H_2S)\) aus einem Gasstrom bei hohen Temperaturen zu entfernen. Es konnte gezeigt werden, dass die Mn-basierten Materialien \(H_2S\) über mehrere Zyklen hinweg entfernen und dabei \(SO_2\) unter oxidativen Bedingungen freisetzen. Ein zweistufiger Mechanismus für die Sulfidierung von Mangan wurde gefunden, der erklärt weshalb \(SO_2\) durch die Reduktion von \(Mn_3O_4\) mit \(H_2S\) erzeugt wird. Diese unerwünschte Nebenreaktion verhindert vollständige Entschwefelung unter den getesteten Bedingungen.

In einem weiteren Schritt wurde die Entfernung von \(H_2S\) und organischen Schwefelspezies durch Molybdänkatalysatoren untersucht. Als Modellsubstanz für organische Schwefelspezies wurde Thiophen \((C_4H_4S)\) benutzt. Es zeigte sich dass der untersuchte Mo/Al_2O_3 Katalysator bei hohen Temperaturen erfolgreich \(H_2S\) und \(C_4H_4S\) über mehrere Zyklen aus dem Gasstrom entfernt. Die Zugabe von Dampf zur Gasphase vermindert allerdings die Reaktivität des Katalysators gegenüber Schwefel aufgrund von kompetitiver Adsorption von \(H_2O\) auf der Katalysatoroberfläche. Dies hindert die Schwefelspezies an der Adsorption, was zu einer Verlangsamung der Reaktion führt.


Acknowledgements

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Chapter 1

Introduction

One of mankind’s earliest energy carriers - wood, has been attracting much interest over the last 5 - 10 years as alternative energy source. Its availability in many parts of the world, the ease of harvesting, its uncomplicated handling, as well as the climate neutrality, are factors that make wood attractive as energy carrier. While there are many different ways to convert wood to energy or fuels, one particularly attractive route is conversion of wood to synthetic natural gas (SNG). SNG, which is essentially methane (CH$_4$), can be stored and transported in the existing infrastructure, and is a transportation fuel with growing acceptance. While being proven feasible in pilot plants, the technology for wood-to-SNG conversion is currently not competitive with fossile natural gas. This is in part due to the required cleaning of the gasified wood at low temperatures, which is necessary before further catalytic conversion.

This work intends to provide knowledge of fundamental mechanisms in high temperature sulfur removal processes, and to elucidate structure-performance relationships of relevant materials. This knowledge will help developing more advanced materials and designing reactors for hot gas cleaning.
CHAPTER 1. INTRODUCTION

1.1 Thermochemical biomass conversion

1.1.1 Using biomass as fuel

Limited reserves of fossil fuels lead to increasing costs for their exploitation. Because of evidence for anthropogenic climate change, alternatives to oil, coal and natural gas as main energy carriers are heavily sought. Biomass is one potential substitute for fossil fuels, since it is abundant in many regions on earth, easy to harvest, and in principle CO$_2$ neutral, as it only releases the same amount of carbon that it captured during the plant’s growth.

However, biomass-derived fuel is currently not economically competitive with fossil fuels, unless technological advances will drive down the price for biomass-derived fuels or electricity, or taxes on carbon emission or similar schemes will be put into place. The goal of this work is to contribute to the improved utilization of biomass, and therefore to lower costs of the biomass-derived fuels.

Types of biomass

The term biomass covers a wide range of natural compounds, with different chemical composition, availability and price. Typically, biomass is divided into two types, according to their moisture content: Dry biomass such as wood, grass, bark or straw, and wet biomass such as sewage sludge, plant residues (from agriculture) or manure. While the boundary value is hard to quantify, van Rossum et al. use the term wet biomass for biomass with more than 70 wt-% moisture. Wet biomass, for which conversion technologies in supercritical water are under development (see for example ref. [2]) is not covered in this thesis.

While the structure and composition of biomass is generally very heterogeneous, dry biomass, which is the focus of this thesis, mainly consists of three molecules: lignin, cellulose and hemicellulose. Typically, wood contains 20 - 30 % lignin, 35 - 50 % cellulose and 20 - 30 % hemicellulose. The three molecules are biopolymers, which behave differently during pyrolysis. Thermogravimetric studies showed that hemicellulose decomposes between 220 and 315 °C with approximately 20 wt- % residues, while cellulose pyrolyses between 315 and 400 °C with almost no residues. Lignin did not show a specific decomposition temperature, but decomposed over the whole temperature range up to 900 °C, with 45 wt- % residues. Differential scanning calorimetry (DSC) revealed that pyrolysis of cellulose is endothermic, while pyrolysis of lignin and hemicellulose is exothermic. Therefore the gasification behaviour of different feedstocks of dry biomass, containing of various contents of lignin, cellulose and hemicellulose, leads to different behaviour during gasification.

Besides the distribution of lignin, cellulose and hemicellulose, different types of dry biomass also vary in their moisture content, ash content and heating values. This is shown in table (1.1). For comparison, bituminous coal is also shown.
1.1. THERMOCHEMICAL BIOMASS CONVERSION

<table>
<thead>
<tr>
<th>moisture content</th>
<th>ash content</th>
<th>lower heating value</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>wheat straw</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>bituminous coal</td>
<td>11</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 1.1: Properties of different biomass feedstocks and coal. [3]

As a consequence of the heterogeneity, the elemental composition, which is shown in table 1.2 is also different.

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood</td>
<td>51.6</td>
<td>6.3</td>
<td>41.5</td>
<td>0</td>
</tr>
<tr>
<td>wheat straw</td>
<td>48.5</td>
<td>5.5</td>
<td>3.9</td>
<td>0.3</td>
</tr>
<tr>
<td>bituminous coal</td>
<td>73.1</td>
<td>5.5</td>
<td>8.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 1.2: Chemical composition (in wt-%) of selected dry biomass and coal [3]

1.1.2 Biomass conversion technologies

The technology that is put into place for conversion of biomass depends on the desired product. For local, small scale generation of heat, such as domestic heating, combustion of biomass is an option with growing popularity, with efficiencies between 78 % and 94 %. [5] Other goals, such as the generation of transportation fuels or cogeneration of electricity and heat, favour a gasification process on a larger scale. For cogeneration (simultaneous generation of heat and electricity), the gasification of biomass can be combined with a gas motor, a gas turbine or a fuel cell. [6] Generation of fuels typically proceeds via syngas chemistry, where the producer gas from the gasifier is catalytically converted to hydrocarbons and / or oxygenates. [7]

Gasification technologies

Gasification is the thermal decomposition of solid matter with understoichiometric air, i.e. without total oxidation to CO₂. This gasification process is divided into four stages: drying, where water is removed from the fuel; pyrolysis, in which volatile compounds are generated; combustion of carbonaceous molecules with oxygen from the gasification medium and finally gasification, where the solid carbon is gasified to carbon monoxide.

In general, fixed bed and fluidized bed gasifiers can be differentiated by the arrangement of the four zones of drying, pyrolysis, combustion and gasification. This is schematically shown in Figure 1.1 where different types of gasifiers with different arrangement of the inlets for fuel and air (as gasification medium) and of the gas outlet are displayed. Fixed bed gasifiers are further
divided into downdraft gasifiers, where the gasification medium flows in the same direction as the fuel, and updraft gasifiers, where the flows of gasification medium and fuel are in opposite direction. In the updraft configuration the combustion takes place at the bottom of the bed and the gasification occurs in an upper region of the bed at rather low temperatures, leading to high tar content in the producer gas. In downdraft gasifiers, the feedstock and the gasification medium flow in cocurrent direction through the gasifier, resulting in higher temperatures at the exit, and thus to lower tar content. Other gasification technologies are entrained flow gasifiers and fluidized bed gasifiers. The latter can be further divided into bubbling beds and circulating beds. As gasification medium, air, oxygen and/or steam are used. A recent review on the generation of SNG gives a broad overview of the different gasification technologies. 

The different gasification technologies have specific advantages and disadvantages. Updraft gasifiers are a simple process with high thermal efficiency, but produce large amounts of tars. Entrained beds generate very low tar content, but require the feedstock to be in a very small size, and are complex to control. Circulating fluidized beds can handle flexible feed rate and

![Figure 1.1: Schematic representation of different gasifier types: updraft (top left), downdraft (top right), bubbling bed (bottom left) and circulating bed (bottom right), from [9]](image)
composition, but present attrition problems.

As of 2001, there were 128 gasification plants with a capacity of 42,000 MW$_{th}$ of synthesis gas in operation worldwide. [11]. These plants are almost exclusively used for gasification of coal. The largest plants are operated by Sasol in South Africa or the Dakota Gasification Plant in the United States. [11]

Catalytic SNG production

Production of Synthetic Natural Gas (SNG) from gasified biomass is attractive mainly for two reasons: first, SNG can be easily stored and transported in the European gas grid, which has a storage capacity of approximately 90,000 mio m$^3$ in Europe (excluding Ukraine), according to Gas Infrastructure Europe, an industry association. [12] This corresponds to approximately 440,000 TWh of energy stored in the grid, assuming storage of CH$_4$ with a lower heating value of 36 MJ m$^{-3}$ at 50 bar. Through the gas grid, energy can be conveniently transported. Second, SNG can be used as transportation fuel, e.g., for cars. It was shown that production of SNG is especially efficient, and therefore economic, if the excess heat can be used locally, as process heat or for domestic heating. [13] To minimize energy consumption and cost of transport, a decentralized infrastructure is preferred, where the wood from local sources is used, and process heat is distributed locally for heating purposes, while the SNG is available all over the gas grid.

1.1.3 The wood-to-SNG process

Over the last decades, various attempts were undertaken to bring technologies for conversion of biomass to SNG to an industrial scale. [8] Generation of SNG from biomass typically contains four steps that are schematically shown in Figure (1.2): gasification, gas cleaning, catalytic methanation and gas upgrading.

![Figure 1.2: Schematic presentation of the SNG production process, modified from [8]](image)

Gas cleaning

The producer gas from the gasifier contains several impurities that need to be removed before further processing. Among them are char (unconverted biomass), ash, tars and sulfur containing
species. Tars are often defined as condensable hydrocarbons with a molecular weight above that of benzene. Among the sulfur species found in biomass producer gas are hydrogen sulfide ($\text{H}_2\text{S}$), carbonyl sulfide (COS), thiophene ($\text{C}_4\text{H}_4\text{S}$), benzothiphene ($\text{C}_8\text{H}_6\text{S}$) and dibenzothiophene ($\text{C}_{12}\text{H}_8\text{S}$). Efficient removal of these impurities is one of the main challenges in further development of the wood-to-SNG process, as will be discussed in greater detail in section (1.1.6).

The first step in gas cleaning is usually filtering of the producer gas directly after the gasification, to remove particulates. To perform the filtration at the high temperatures of the gasification (approximately 800 °C) is challenging for filter materials, but is crucial for a gas cleaning process chain that operates at high temperatures. This hot gas filtration can eventually be combined with catalytic gas cleaning, which is called reactive hot gas filtration. This was shown to convert 58 % of the tar content, using filter candles with Ni as catalyst, supported on MgO – Al$_2$O$_3$. 

### Catalytic methanation

Under the conditions in a methanation reactor, three reactions are dominant:

\[
\text{Methanation} \quad \text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (1.1)
\]

\[
\text{Water-gas shift} \quad \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (1.2)
\]

\[
\text{Boudouard} \quad 2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \quad (1.3)
\]

Since the ratio of $\text{H}_2 : \text{CO}$ in biomass is typically lower than three, which is required for reaction (1.1), steam can be added to the feed, from which $\text{H}_2$ is generated by reaction (1.2) consuming CO. Excess CO can form adsorbed carbon by reaction (1.3), which is usually undesired, as it can lead to catalyst deactivation by carbon deposition.

Different metals were compared for their methanation activity. Ni, which is commonly used for methanation showed rate constants comparable to Ru and Rh. Due to its low price, Ni is typically the element of choice for methanation. The reaction mechanism of a Ni methanation catalyst was studied extensively before. It was proposed that $\text{H}_2$ and CO adsorb dissociatively on the Ni surface, and the surface C is stepwise hydrogenated to $\text{CH}_4$. 

State of the art for methanation are fixed bed reactors. However, it was found that Ni catalysts are prone to carbon deposition, especially in the presence of acetylenes or olefins. In a fluidized bed, carbon deposition on the catalyst was largely absent, which was attributed to internal regeneration. Sulfur is also known to poison the activity of Ni or Ru methanation catalysts. This is why upstream desulfurization is necessary.
1.1. THERMOCHEMICAL BIOMASS CONVERSION

**Gas upgrading**

Before the generated SNG can be injected into the gas grid, it needs to be upgraded. This step mainly consists of removal of CO$_2$ and water. CO$_2$, which is generated in the water-gas shift reaction (equation (1.2)), can be removed by amine scrubbing $^{25}$ or pressure swing adsorption. $^{26}$ Water is removed by condensation. Finally, the SNG must be odorized and pressurized for injection into the gas grid.

1.1.4 Economics of the Wood-to-SNG process

At the current stage, the economics of the Wood-to-SNG process are not fully clear, because of two reasons: first, the price of the fuel varies strongly over time and place. Second, the technology is not yet fixed, as there are still many options and developments, a few of which this thesis aims to provide. However, broad trends can be extracted from the available information.

The price for wood varies over time, countries and the various types of wood (bulk wood, pellets, chips etc.). For wood pellets in the industrial markets the price range was between 6 and 14 € GJ$^{-1}$ over different European countries between 2006 and 2010. For wood chips, the price range was 2 - 7 € GJ$^{-1}$ from 2006 to 2010. $^{27}$

Thermo-economic analysis of the SNG production from biomass, considering various process options, showed that a production cost of 76 - 107 € MWh$^{-1}_{SNG}$ can be expected for a plant with a capacity of 20 MWh$^{thermal}_{SNG}$. $^{28}$ By contrast, the average price for natural gas at the European Energy Exchange (EEX) in 2012 was 24,66 € MWh$^{-1}$. $^{29}$

Even though the price for fossil natural gas and wood vary strongly over different regions worldwide, it is clear that SNG is currently not economically competitive with fossil natural gas. Technological solutions to reduce the costs are therefore required. Techno-economic analysis of a biomass to ethanol process showed that current technology for gas cleaning (tar reforming, acid gas and sulfur removal) represents 31% of the minimum selling price of the produced ethanol. $^{30}$ The aim of this thesis is to contribute to efficient gas cleaning, in order to ultimately improve the economics of SNG.

1.1.5 Demonstration and commercial plants

While there is much research on the lab scale, only few large scale gasification plants for conversion of biomass to SNG exist so far. In Güssing (Austria), a process development unit using the Fast Internally Circulating Fluidized Bed (FICFB) gasification technology with 1 MW$_{SNG}$ output was installed. This process is schematically displayed in $^{13}$.

In Gothenburg (Sweden), the GoBiGas project aims at 100 MW$_{SNG}$ output, which will be reached in two stages. First, a 20 MW plant is being erected and shall be operational in late
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Figure 1.3: Schematic presentation of the Güssing PDU, from [8].

2013. It is planned to be extended with two 40 MW plants if the 20 MW plant is successful. [31]
Since it is a commercial project, only very little technical information is available in the open literature.

1.1.6 Major challenge for the Wood-to-SNG process: gas cleaning

In virtually all biomass, as well as in coal and other fossil fuels, impurities are present (see also table 1.2) that need to be removed during processing. Among these impurities, sulfur plays an important role because it is corrosive to plant equipment, environmentally disadvantageous, and chemically poisonous to metal catalysts that are used for methanation, reforming or other catalytic processes.

In Coal-to-SNG plants, sulfur is typically removed by scrubbing, where the hot gas from the gasifier is cooled down and washed with a liquid (see next section). During scrubbing, steam in the producer gas is also condensed. Afterwards, the cleaned gas is heated again for methanation to 300 - 400 °C, and steam is added for adjustment of the H₂ : CO ratio, using the water-gas shift reaction \( \text{1.2} \).

Scrubbing represents a major cost factor in the overall wood-to-SNG process, because of the scrubbing equipment, the heat exchangers and workup of the scrubbing liquid. In addition, process efficiency is decreased due to incomplete heat recovery. As a consequence, ways to replace scrubbing with more efficient methods for gas cleaning are required.
Hot gas cleaning describes generally a process in which the producer gas from the gasifier is cleaned at temperatures between that of the gasifier, and that of the methanation reactor, thus saving the intermittent condensation step. A technoeconomic analysis of the Wood-to-SNG process showed that hot gas cleaning can improve the chemical efficiency $\epsilon$ by three to five percentage points.\[32\] Chemical efficiency is defined in this study as the ratio of energy output (as SNG, electricity and heat) by energy input (as biomass and solvent for scrubbing).

State of the art: cold gas cleaning

State of the art for the gas cleaning is scrubbing at low temperatures. Several approaches exist for this: \[33\] the Selexol process uses polyethyleneglycol at -4 to -7 °C, removing up to 99% of $\text{H}_2\text{S}$. Methanol is used in the Rectisol process at -35 to -60 °C, removing up to 99.9 % $\text{H}_2\text{S}$ and 98.5 % $\text{CO}_2$. Methyl-diethanolamine (MDEA) is used to adsorb $\text{H}_2\text{S}$ at ambient conditions. After the cold scrubbing, ZnO beds can be used to remove residual amounts of $\text{H}_2\text{S}$ by conversion of ZnO with $\text{H}_2\text{S}$ to ZnS and $\text{H}_2\text{O}$.\[34\]

As scrubbing is performed at low temperatures, steam in the producer gas is condensed. Adjustment of the $\text{H}_2 : \text{CO}$ ratio to a value of three (see reaction (1.1)) is typically required for the methanation process, and is achieved by means of the water-gas shift reaction (1.2), which necessitates the evaporation of water after the cold scrubbing. This evaporation, together with the heat exchangers for cooling and heating of the gas, and the regeneration of the scrubbing liquid with steam, present costs, which need to be avoided in order to make the wood-to-SNG process competitive.

Approaches for hot gas cleaning

To reduce the investment and operational cost of wood-to-SNG plants, hot gas cleaning of producer gas is considered an important factor to improve economic feasibility of SNG production from biomass. The concepts for hot gas cleaning can be roughly divided into two groups: concepts that want to avoid catalyst poisoning in the first place, and therefore try to remove all poisons before the methanation, and those concepts that accept catalyst poisoning and seek to regenerate the catalyst efficiently.

Sulfur removal concepts The first group of concepts that try to avoid sulfur poisoning can be further subdivided into concepts that try to enhance existing unit operations with gas cleaning properties, and concepts that include an additional, dedicated gas cleaning reactor.

Integrating gas cleaning into existing unit operations typically requires materials development, e.g. by trying to make the methanation catalyst sulfur tolerant, or adding catalytic properties to the gasification bed. Several authors and patents (e.g. \[35\]) describe the use of sulfur tolerant
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methanation catalysts in fixed beds to convert mixtures from high temperature coal gasification containing carbon monoxide, hydrogen and sulfur compounds to methane. However, none of them showed that the catalyst would be active in the presence of olefins or even aromatic compounds in the feed gas. Such compounds are routinely found in synthesis gas from a low temperature gasifier. Catalysts for sulfur tolerant methanation are for instance molybdenum sulfide or vanadium sulfide. \cite{36,37} However, sulfur-tolerant methanation is typically operated at much higher $H_2$ partial pressures compared to those in an atmospheric gasification process. A simplified concept for the wood-to-SNG process accepts the deactivation of the Ni methanation catalyst, which is also used for tar reforming, thereby reducing size, complexity and investment for the SNG plant. \cite{38}

Dedicated gas cleaning reactors typically contain a material, often a metal oxide, that is transformed into a sulfide, thereby removing sulfur from the gas stream. This process comes to an end when all the available material is in the sulfide form, and therefore needs to be regenerated. In the literature, the focus is mostly on the removal of $H_2S$ from the gas, and extensive reviews can be found in \cite{39,41}. A different approach for dedicated gas cleaning was proposed by Rabou and Bos. They describe the use of a commercial molybdenum based hydrodesulphurization (HDS) catalyst to convert thiophenes etc. to hydrogen sulfide ($H_2S$) which is followed by $H_2S$ removal by means of a metal oxide bed (ZnO) and subsequent methanation over a nickel catalyst. \cite{42} However, the authors mention very high costs due to the low activity of the catalyst in their process chain.

\textbf{Catalyst regeneration} Protocols for regeneration of sulfur poisoned methanation catalysts are another option, which would make dedicated gas cleaning reactors or materials unnecessary. Regeneration is performed either during shutdown of the plant, or by installing multiple catalyst beds, of which some are regenerated while others are in use.

Katzer et al. describe a process for regeneration of sulfur-poisoned Ni methanation catalysts by exposing the catalyst to a diluted oxygen/inert-gas mixture. \cite{43} They use very low oxygen concentrations of 1-10 ppm to regenerate a Ni catalyst at temperatures between 300 °C and 500 °C. The low oxygen content most probably shall help to avoid the formation of a nickel sulfate phase which is very stable and would deactivate the catalyst completely. However, the low oxygen content leads to very long regeneration times (several tens of hours).

Johnson describes a process for synthesis of hydrocarbons from natural-gas derived synthesis gas where a sulfur poisoned iron catalyst is regenerated in an oxidizer and reduced in a reducer, before being returned to the synthesis reactor. \cite{44} Carr describes a method of regeneration of sulfur poisoned hydrocarbon cracking catalysts (Co, Ni, W, Cu, Mo, Cr, Mn, V or their oxides) consisting of several cycles of oxidation and subsequent reduction. \cite{45}

The regeneration of nickel catalysts was tested by Aguinaga and Montes using a sequence of oxidation- and reduction steps at constant temperature between 200 °C and 500 °C. \cite{46} The
catalysts were poisoned by thiophene and the regeneration procedure with very low O₂ concentration (0.05 vol-%) removed up to 80% of the sulfur in 26 minutes and led to complete reactivation. Li et al. describe the regeneration of sulfur-poisoned nickel steam reforming catalysts with an oxidation- and a reduction step. The proposed temperatures are above 750 °C for the oxidation in diluted oxygen, and above 850 °C for the regeneration in inert gas and subsequent reduction in diluted hydrogen which is far above the temperature limit for a typical methanation catalyst (300 - 400 °C).

**Choice of materials** Innumerable options exist for selecting materials that remove sulfur by sorption and / or reforming. Even restricting the choice to classical metals or metal oxides on an oxide support leaves many possible elements. Combining these to binary, ternary or even quarternary mixtures leads to even more possible materials. To restrict the number of elements to be tested, the following list of criteria was established, that the material should fulfill.

- Uptake of H₂S and COS under reducing conditions and release under oxidizing conditions
- Catalytic conversion or uptake of organic sulfur compounds (thiophenes)
- Stability in a temperature range between 300 °C and 800 °C
- No volatization of the metal under the reducing and oxidizing conditions
- Stability over many redox cycles, i.e. no sintering or permanent deactivation

In this thesis, three concepts will be investigated, which make use of metal (-oxides) which fulfill these requirements.

- Bulk sulfur removal over Mn-based materials, which could be employed directly in the gasifier (chapter [3]).
- Removal of H₂S and organic sulfur species over supported Mo catalysts, which could be implemented in a stand-alone gas cleaning reactor (chapter [4]).
- Integrated methane synthesis and removal of H₂S and organic sulfur species over the same material (a supported Ru catalyst), which could replace a gas cleaning unit and the methanation reactor (chapters [5] and [6]).

The goal of this thesis is to provide options for high temperature desulfurization of biomass-derived producer gas, that allow generation of SNG from wood at lower costs and/or with increased efficiency. To this end, three concepts for high temperature desulfurization are proposed and the mechanisms for sulfur removal are investigated. To study these mechanisms, information about the structure of the solid materials and their reactivity is desired. The reactivity is studied by mass spectrometry (MS) or gas chromatography (GC). To investigate the structure of the solid samples, different methods are at hand.
1.1.7 Methods for probing the structure of solid samples in situ

There are a number of techniques available to study the structure of solid samples, each with individual advantages and limitations. Most of these techniques are based on interaction of electromagnetic radiation with solid matter.

Infrared (IR) spectroscopies probe vibrations of those molecules whose molecular dipole moment changes due to the excited vibration. This includes for instance CO, CO$_2$, H$_2$O or CH$_4$. If the molecules are adsorbed on a catalyst surface, the vibrational frequencies change due to the interaction with the surface, and these changes can be detected in the IR spectra. The state of the solid catalyst is however usually not probed by IR spectroscopies.

X-ray photoelectron spectroscopy (XPS) probes the occupied orbitals of the sample. The X-rays create photoelectrons that are analyzed according to their energies, which can be related to the electron’s binding energies. Due to the low penetration depth of electrons, XPS is a surface sensitive technique, that is usually performed at very low pressures. Recent developments in differential pumping allow in situ XPS experiments,\cite{48,50} while the absolute gas pressures are still far below those that are accessible with other X-ray based techniques.\cite{51}

X-ray crystallography, or X-ray diffraction (XRD) determines the structure of crystalline samples, based on Bragg’s law. XRD typically probes the bulk of the sample, irrespective of the sample’s element. Information on particle size can be derived from the Scherrer formula,\cite{52} given that the particles are large enough (larger than $\sim 2$ nm) to be detected by XRD.\cite{53}

X-rays can also be used for spectroscopy, where they probe elements of choice. In X-ray absorption spectroscopy (XAS), the energy of the X-ray photons is varied to measure the sample’s absorption coefficient as function of energy. In contrast to XRD, XAS does not require crystalline samples, and is not limited by the particle size of the element of interest. This makes it an excellent tool for investigation of catalysts, which often have very small particle size (from clusters of a few nm down to single atoms).
1.2 X-ray absorption spectroscopy

In this section, fundamentals of X-ray absorption spectroscopy, which is the main technique that was used in this thesis, are discussed. First, the fundamental processes that give rise to the X-ray absorption spectrum, and the basic data treatment will be described. This section will be concluded by a description of current challenges in XAS, especially with respect to catalysis research, which is the sensitivity of XAS.

1.2.1 X-ray absorption

To determine the X-ray absorption of a sample, the intensity of the X-ray beam is measured before the sample and after the sample. The transmitted intensity $I_t$ is:

$$I_t = I_0 e^{-\mu d}$$

where $I_0$ is the beam intensity before the sample, $\mu$ is the absorption coefficient (or absorbance) of the sample, and $d$ is the sample’s thickness. Rearrangement allows calculating the absorption coefficient as a function of sample thickness and the measurable intensities before and after the sample:

$$\mu d = \ln\left(\frac{I_0}{I_t}\right)$$

This relation is true for every kind of homogeneous sample, be it gaseous, liquid or solid. Furthermore, the absorbance is influenced by the elemental composition of the sample, since heavy elements absorb more radiation than light elements. When the energy of the X-rays is scanned, the absorption coefficient changes drastically at specific energies. The energies at which this happens depends on the sample’s electronic structure.

1.2.2 Physical background

When a photon hits an atom, it can interact with the atom’s electrons. If the photon energy matches the energy difference between an electron’s binding energy and the energy of an unoccupied state, the photon is absorbed and will excite the electron into the unfilled orbital. This is schematically shown in Figure 1.4.

If the energy of the incoming photon is higher than the binding energy, the electron will become a photoelectron, with a kinetic energy that equals the difference between the binding energy and the photon energy. The corresponding photon energy is called the absorption edge, typically associated with the energy level of the electron, i.e. K-edge for photon energies matching the binding energies of electrons in the K-shell.
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Figure 1.4: Schematic energy diagram of K-edge XAS: the incoming photon excites a 1s electron to an energy above the Fermi energy ($E_f$), creating a core hole. The core hole is filled, e.g. by a 2p electron, while the energy difference between the 2p and the 1s level is the energy of the fluorescent photon.

Near-edge structure

A XAS spectrum at the Cr K-edge is shown in Figure (1.5), where the normalized absorption coefficient is plotted against energy. The absorption coefficient increases at around 5990 eV, which is the binding energy of an 1s electron of Cr. The region of the XAS spectra at energies around the absorption edge are called X-ray absorption near-edge structure (XANES). This part of the spectrum gives information on the electronic structure of the absorber atom, such as oxidation state or unoccupied electronic states. XAS spectra can show features before the absorption edge, so called pre-edge features. Those indicate transitions of the electron to higher, unoccupied orbitals below the Fermi level. The position of the edge itself is an indication of the oxidation state of the absorbing atom. Higher oxidation states require more energy for an additional electron to be released, resulting in higher edge energies.

A semi-quantitative analysis of the sample’s composition is possible, based on the fitting of the XANES spectrum with a linear combination of spectra of reference compounds. This is shown in Figure (1.5), where a Cr sample of unknown composition is fitted with two reference compounds, Cr$_2$O$_3$ and K$_2$Cr$_2$O$_7$. While it was known that the sample contained the two compounds, their ratio was determined by linear combination fitting.

Linear combination fitting (LCF) does require that spectra for reference compounds exist. Moreover, linear combination fitting of a sample with unknown composition requires that it is known which reference spectra can be used. To determine the best fit of the data with correct reference spectra, statistical analysis can be used. The accuracy of LCF is typically on the order of ± 5 %.

Ab initio simulations can be used to simulate XANES spectra of pure compounds. These
1.2. X-RAY ABSORPTION SPECTROSCOPY

Figure 1.5: Cr K-edge XANES spectrum of a sample, with linear combination fit (dashed line) of two references, Cr$_2$O$_3$ (green) and K$_2$Cr$_2$O$_7$ (orange) weighted by the fitted fractions.

computational methods provide many insights into the sample’s electronic structure. Recently, methods for parametrized calculations of XANES spectra were developed.\textsuperscript{[57,58]} This allow for fitting of XANES spectra based on calculations of the spectra with full multiple scattering codes to extract structural information, and does not rely on experimental references.

Extended range structure

At 50 - 100 eV above the absorption edge, solid or liquid materials exhibit an oscillatory structure in the XAS spectrum. This is called the extended X-ray absorption fine structure (EXAFS) region, and this part of the spectrum carries a wealth of structural information.

When the photon energy is higher than the binding energy of the core electron, the electron is released from the atom as a photoelectron, having a kinetic energy that equals the difference between the energy of the incoming photon and the binding energy:

$$E_{\text{kinetic}} = E_{\text{photon-in}} - E_{\text{binding}}$$  \hspace{1cm} (1.4)

This photoelectron then scatters at the neighbouring atoms, and is eventually scattered back to the absorber. Thus, it probes the local environment around the absorbing atom. From the point of view of the absorbing atom (i.e. the atom where the photoelectron is created), the surrounding atoms are divided into scattering shells (see Figure (1.6)), according to their distance to the absorber, the atomic weight of the scattering atoms, and the number of atoms with the same element at the same distance (coordination number).

The EXAFS signal $\chi$ can be extracted from the data by normalizing the data to a structureless
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Figure 1.6: Two-dimensional representation of a square lattice, with the central absorbing atom, and the two nearest scattering shells. Both shells have a coordination number of 4. Single scattering is shown as red lines, multiple scattering is shown as blue lines.

The background function $\mu_0$: 

$$\chi = \frac{\Delta \mu}{\mu_0}$$

The EXAFS signal can be described by the following formula: 

$$\chi(k) = \sum N \cdot S_0^2 \cdot \frac{F(k)}{k \cdot R^2} e^{-2k^2\sigma^2} e^{-2R/\lambda k} \sin(kR + \Phi)$$ (1.5)

In the so-called EXAFS equation, the EXAFS signal $\chi$ is the sum of all scattering paths. Instead of the kinetic energy, the signal is typically shown as a function of the wavevector $k$, where $k = 2(m_e(E - E_{kin})/\hbar)^{1/2}$ with the electron mass $m_e$ and the reduced Planck constant $\hbar$. Each scattering path is described by the coordination number $N$, the according pseudo Debye-Waller factor $\sigma^2$ and the radial distance $R$. The pseudo Debye-Waller factor represents structural disorder, caused for example by thermal motion. In addition, the backscattering amplitude $F(k)$, the phase shift $\Phi$, the electron mean free path $\lambda$ and the amplitude reduction factor $S_0^2$, which originates from inelastic interaction of the photoelectron with the absorbing atom, are taken into account. The backscattering amplitude and the phase shift can be calculated with ab initio methods.

From equation (1.5), it becomes clear that the EXAFS signal is amplified by more atoms in the coordination shell (i.e. higher $N$). At higher values of $R$ and $k$, the signal is damped, so that EXAFS probes a radius of $\sim 6$ Å around the absorbing atom.

Data treatment

Extraction of the EXAFS signal $\chi(k)$ contains three steps: normalization, background subtraction, and Fourier transformation, which are usually performed by specialized software, such as IFEFFIT. These steps are schematically displayed in Figure 1.7, where the raw data is
normalized such that the absorbance at energies below the absorption edge is zero, and the absorbance at energies above the edge is oscillating around 1. Next, the EXAFS signal is extracted by subtracting a smooth background function from the normalized spectrum, representing the signal of an atom with no neighbours, followed by transforming the photon energy $E$ into the wavenumber $k$. Note that the function is here multiplied with $k^2$ to amplify the parts in the spectrum at higher values of $k$, where the signal is damped. Finally, the EXAFS signal is Fourier transformed, yielding a complex function. [60] Shown here are the magnitude and the real part of the Fourier transformed EXAFS function.

The Fourier transform of the EXAFS signal is a pseudo radial-distribution function (RDF, see Figure 1.7d), which contains information on the nature of the atoms surrounding the absorbing atom, its number and distances. In this example of a MoS$_2$ sample, the first peak at approximately 1.8 Å corresponds to the Mo-S scattering shell, and the peak at approximately 2.9 Å corresponds to the first Mo-Mo scattering shell. Note that the Fourier transform here is not phase corrected so the apparent distances are not the real atom distances. The phase shift is represented in the EXAFS equation (1.5) in the sine function, and it depends on the scattering element and the wavevector $k$. [61] The information on coordination number and radial distance is extracted by fitting the experimental data to a theoretical model, which can be based upon a theoretical crystal structure, and calculated numerically, for instance with the FEFF code. [63]
EXAFS fitting

To extract information on the sample’s geometry, such as the type of elements surrounding the absorbing atom, their coordination number (N), distance (R) and pseudo Debye-Waller factor ($\sigma^2$), the EXAFS signal $\chi(k)$ is fitted to a theoretical model. This can be done for instance with IFEFFIT [62] and the ARTEMIS software. [64] A structure model (e.g. from the ICSD - Inorganic Crystal Structure Database) is converted to an input file for FEFF [63]. From this, FEFF calculates theoretical scattering paths around the chosen absorbing atom, with their respective coordination number, bond distance and scattering amplitude and phase. The model is essentially a function like the EXAFS function (Equation (1.5)). In this function, there are five free parameters: the coordination number N, the amplitude reduction factor $S_0^2$, the radial distance R, the Debye-Waller factor $\sigma^2$ and a correction term for the edge energy $\Delta E_0$. Since N and $S_0^2$ are correlated, one of them needs to be fixed. Typically, $S_0^2$ is derived from a fit of a spectrum of a reference material, and then fitted for the fit of the sample. The software (e.g. IFEFFIT) then runs a minimization routine, so that the difference between the data and the model (e.g. expressed as $\chi^2 = \frac{N_{idp}}{N} \sum_{i=1}^{N} \left( \left| Re(f_i) \right|^2 + \left| Im(f_i) \right|^2 \right)$) is minimized, i.e. the variables are changed such that the model fits to the data. In the expression of $\chi^2$, $f_i$ is the complex function that is to be minimized with its real and imaginary part, N is the number of functions, $N_{idp}$ is the number of independent points in the data, and $\epsilon$ is the uncertainty of the function. The number of independent points $N_{idp}$ depends on the data range in k-space and in R-space, that is included into the fit: $N_{idp} = \frac{2(k_{max} - k_{min})(R_{max} - R_{min})}{\pi} + 2$. For the fit to be reliable, it is best practice to keep the number of free parameters in the fit at less than half of $N_{idp}$. This means that a large region in k-space allows more fit variables, i.e. good spectra quality up to high k-values is required for more complex fit models. In principle, the fit can be carried out in k-space or R-space (i.e. before and after Fourier transformation). Doing the fit in R-space has the advantage that single scattering shells can be selectively fitted by multiplying a window function around the peak of choice, filtering out the rest of the data. [59]

In order to reduce the number of free parameters of the fit, the parameters must either be fixed, or be related to each other. For instance, it is common practice to set the parameter $\Delta E_0$ the same for all fitting paths. Furthermore, relations between parameters can be implemented, that further reduce the number of parameters. This could be for instance the assumption of isotropic expansion / contraction, that would allow a relationship between the bond distances R of different fitting paths.

To study the accuracy of EXAFS fitting, Cramer et al. studied Mo complexes using EXAFS, and found that fitting of multiple-shell models was accurate within 19 % of coordination number N, and 0.03 Å in radial distance R. [65] Comparing experimental data with calculated spectra, Li et al found that the error for coordination number is generally < 10 % and for distance the error is ~ 0.005 Å. [66]
1.2.3 Layout of typical in situ XAS experiments

A simplified layout of a beamline for X-ray absorption spectroscopy is shown in Figure 1.8. The polychromatic X-ray beam coming from the storage ring is reflected on a mirror to collimate the beam and absorb a portion of the heat load. In a monochromator, which is typically a parallel set of crystals, the beam is monochromatized, i.e. a specific wavelength is selected. Another mirror focuses the beam. In the experimental hutch, the beam passes the first ionization chamber $I_0$, to measure the incident beam intensity. After the sample, which is depicted here as a tubular reactor filled with a catalyst, the beam intensity is measured with another ionization chamber $I_1$. For energy calibration, a metal foil is often used after $I_1$ and before another ionization chamber $I_2$. Ionization chambers are gas-filled chambers with two parallel electrodes. Between the electrodes, a static high voltage is applied. The X-rays ionize a fraction of the gas, and the ions are collected at the anode, and the current is measured.

![Diagram of in situ XAS experiment](image)

**Figure 1.8:** Schematic depiction of an in situ XAS experiment. X-rays from the synchrotron are monochromatized and aligned with the heated reactor. In the reactor, various gases are mixed for heterogeneous catalysis experiments. The beam intensity is measured before and after the sample, and after a reference sample.

For heterogeneous catalysis or gas-solid experiments, as they are shown in this thesis, a reactor is used, which needs to be temperature resistant and X-ray transparent. For conditions at modest pressures (around atmospheric pressure), quartz capillaries are often used. The reactor is filled with the sample, heated to the desired temperature, and a gas mixture of interest is passed over the sample. Simultaneous measurement of the reactivity by gas analysis at the reactor outlet, and the structure by XAS, allows mechanistic insights in the reactions at the interface of the gas phase and the solid sample.


1.2.4 Challenges to XAS: Sensitivity

As hard X-rays typically have a penetration depth that is much larger than the size of single catalyst particles, the resulting spectrum is an average over many particles. Consequently, the sensitivity of XAS towards changes in the particle’s structure is dominated by the particle size distribution; This is schematically shown in Figure 1.9, where two 2-dimensional atom clusters are compared. On the left side, a 19-atom cluster is shown, of which 12 atoms are exposed to the surface. Hence, its dispersion is $\frac{12}{19} = 0.63$. On the right side, a 91-atom cluster is shown, of which 30 atoms are exposed to the surface, resulting in a dispersion of $\frac{30}{91} = 0.32$. On both clusters, a second species is adsorbed with the same surface coverage of 50%. As a consequence of the differences in dispersion, the XAS spectrum of the 19-atom cluster will consist to $0.5 \times 0.63 = 0.31 = 31\%$ of atoms that are bound to the adsorbed atom. On the 91-atom cluster, only $0.5 \times 0.32 = 0.16 = 16\%$ of the atoms are bound to the adsorbed atom. This schematic illustration shows that changes in the catalyst’s structure, induced for instance by adsorption of molecules on the catalyst’s surface, will be much clearer visible in the spectra of the small particles.

![Figure 1.9: Schematic comparison of a small 19-atom cluster with a 91-atom cluster. On both clusters’ surfaces, another species is adsorbed with the same coverage](image)

Furthermore, the sensitivity of XAS, and in fact every measurement, is determined by the signal to noise ratio of the measured data. While measurement of reference compounds is typically optimized to get an ideal signal to noise ratio, data quality of real systems, such as supported catalysts, is often below optimum. This can be because, for instance, the catalyst has a low loading of the active metal (such as noble metals), or the metal is embedded in a strongly absorbing matrix, such as oxides of high-Z elements. Another possible reason for low data quality is a desired high time resolution, which only allows for accumulation of low doses of X-rays on a detector.

For these reasons, it is desirable to enhance the sensitivity of XAS for systems which show only small changes compared to the bulk structure, and for systems that have poor data quality.
Chapter 2

Quantification of modulated excitation X-ray absorption spectra

2.1 Abstract

The sensitivity of X-ray absorption spectroscopy (XAS) can be increased by using the modulated excitation approach, where the sample is excited with a periodic external stimulation (e.g. changes in temperature, gas/liquid concentration, etc.) and the spectra are filtered with the frequency of the excitation. The resulting demodulated spectra contain similar spectral features as difference spectra, but to much higher k values, due to the isolation of the structural change that occurs with the same frequency as that of the excitation. Furthermore, multiple intermediate species that occur with a phase delay can uniquely be differentiated. In this chapter, a robust approach for the quantitative analysis of demodulated extended X-ray absorption fine structure (EXAFS) spectra is developed. Simulations show that the proposed fitting approach resolves small changes in the sample’s structure, with greatly enhanced precision. Experimentally, this is demonstrated by the quantification of of ruthenium oxide species formed upon partial oxidation of a Ru metal particle, which can not be detected in a standard EXAFS experiment.

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The Ru/Al₂O₃ sample that was used in this chapter was prepared by Thanh-Bin Truong at PSI. Evgueny Kleymenov wrote parts of the Matlab script that was used for data analysis of the demodulated spectra in this and the following chapters.
2.2 Introduction

2.2.1 Improved sensitivity of XAS

Due to the large penetration depth of hard X-rays, analysis of EXAFS yields the average structure around all atoms of the element of interest within the sample. Often however, it is a small fraction of atoms that are the species of interest; they may thus escape accurate detection using XAS. This is, for example, the case in heterogeneous catalysts, where only a minor fraction of atoms contributes to catalytic conversion. A method that is able to quantify structural information only of the fraction of atoms that is involved in a reaction is therefore required.

The fitting precision of experimental EXAFS data to theoretical models and experimental standards was examined by Li et al. [66] By systematically varying the structural parameters, Li et al. mapped the difference between fit and experimental data for a range of experimental standards. They concluded that the fitting errors in a typical EXAFS fit for coordination numbers are generally < 10% and the error for the nearest-neighbor distance is typically ∼ 0.005 Å. Accordingly, the presence of a small fraction of atoms that has a different coordination sphere is easily lost in conventional EXAFS analysis.

The sensitivity of the structural parameters derived from EXAFS fitting can be improved by using difference spectra, obtained under stable experimental conditions (such as stable X-ray optics and chemical stability). Pettifer et al. reported sensitivity to distances of 1 femto-meter in a magnetostrictive experiment under stable experimental conditions, when analyzing the difference spectra between different magnetization directions. [68]

Difference spectra have also been used in ultra-fast XAS experiments on metal complexes, where the bond distance changes upon laser excitation, while only a small fraction of atoms gets excited by the laser. In the approach by Benfatto et al, theoretical difference spectra (between the ground state and various scenarios for the excited state), calculated with the MXAN software, are fitted to the experimental difference spectrum (between the ground state and the excited state) in energy space. [69] Finally, the ∆μ-XANES technique uses difference X-ray absorption near edge structure (XANES) spectra to distinguish small spectral changes and identify their origin, for instance due to adsorption of reactants and intermediates on catalyst nanoparticles. [70]

2.2.2 Concept of modulated excitation

Modulated excitation spectroscopy (MES), also called phase sensitive detection, offers the possibility to pick up small changes in structural parameters, and those of only the fraction of atoms that change with the modulation frequency. In a modulated excitation experiment, a sample is excited with a periodically alternating external stimulation such as temperature, pressure, magnetic field, pH, potential and concentration. The measured system response, in this case
the time-resolved XAS spectra, is then filtered with the excitation frequency. Mathematically a modulated excitation experiment is described by equation (2.1): \[ A_k^{\Phi_{PSD}}(E) = \frac{2}{T} \int_0^T A(E,t) \sin(k\omega t + \Phi_{PSD}^k) \, dt \] (2.1)

where \( A(E,t) \) is the original signal (i.e. the XAS spectrum) as a function of time \( t \) and energy \( E \), \( k = 1 \) is the fundamental harmonic, \( \omega \) is the frequency of the external stimulation, \( \Phi_{PSD}^k \) is the demodulation phase angle and \( T = 1/\omega \) is the modulation period. By calculating the demodulated spectrum \( A(E) \) for phase angles between 0 and 360°, the spectra are transformed from the time-domain into a phase-domain. This mathematical procedure cancels out all parts of the measured spectra that do not follow the excitation frequency \( \omega \). These parts include the spectator species and noise. In other words, MES contains only the signal of the changes imposed by the external stimulus. Compared to difference spectra, the data quality of demodulated spectra is greatly improved, because noise is filtered out. In addition, the demodulation procedure yields all difference spectra that occur due to the stimulation, by simply varying the phase angle \( \Phi_{PSD}^k \). Therefore, multiple intermediate species that occur with a phase delay, (e.g. oxidation or reduction via multiple oxidation states) can in principle be differentiated. When the spectra only show two distinct states, the demodulated spectra will show the same spectral features as the difference spectrum of spectra of these two distinct states, only with much less noise. The modulated excitation approach has been applied to infrared spectroscopy, \[71, 73\] Raman spectroscopy and to X-ray diffraction (XRD), \[74, 76\] where a correlated temporal analysis of the Raman and the XRD signals allowed a more detailed study of phase transitions. Recent modulated excitation XAS experiments showed the feasibility of recording demodulated XAS spectra. \[77, 79\] These studies demonstrated that minority species can be identified in modulation excitation XAS. So far, the analysis of demodulated XAS spectra has been limited to fingerprinting demodulated spectra to known reference spectra.

**Organization of this chapter**

In this chapter, a method to quantitatively analyze demodulated XAS spectra is proposed, thus fully exploiting the information that is contained in the demodulated XAS spectra. A fitting approach to extract quantitative structural parameters from demodulated XAS spectra is developed. The robustness and sensitivity of the fitting approach is systematically investigated with simulated difference spectra. Demodulated spectra contain the same information as difference spectra, only with improved signal-to-noise (S/N) ratio, i.e. less noise. \[77, 79\] For the theoretical analysis, the discussion is limited to a simple one-step reaction, where the reaction occurs instantaneously. Extension of this approach to more complex schemes can be found in chapter (5.3.5). Therefore, a fitting approach for difference spectra between the two states also works on demodulated spectra. Different S/N ratios were investigated to show how the mini-
mum attainable fitting values depend on data quality. The S/N ratio of demodulated spectra can experimentally be improved by repeating the stimulation multiple times and optimizing the sample’s absorption coefficient so that $\mu_d = 2.55$, which yields ideal S/N ratio. [59]

Finally the fitting approach developed here is tested on an experimental dataset where a 2 wt% Ru/Al$_2$O$_3$ catalyst is periodically reduced and partially oxidized. It is shown that modulated excitation XAS allows resolving small structural differences which are lost in regular EXAFS analysis of full spectra and of difference spectra, because the S/N ratio of demodulated spectra is higher than that of difference XAS spectra and because the species that reacts to the stimulation is filtered out from unreactive spectator species.
2.3 Theoretical approach

To assess the robustness of the fitting approach, it is tested with a set of simulated spectra. Since the scope of this chapter is quantitative fitting of demodulated spectra in general, without regard of the dynamic information that is also enclosed in the demodulated spectra, difference spectra were simulated, since they contain the same structural information as demodulated spectra. Due to that similarity, demodulated spectra will be discussed in the following, while the data was generated by calculating differences of full EXAFS spectra. To understand the contribution of the different structural parameters to demodulated EXAFS spectra, K-edge spectra of metallic ruthenium, consisting only of the first Ru-Ru shell, were simulated with the ab initio multiple scattering program FEFF 6.0. This Ru-Ru shell, called $\chi_a$, had a nominal distance (R) of 2.6657 Å, a coordination number (N) of 12 and a pseudo Debye-Waller factor ($\sigma^2$) of 0.003 Å$^2$. A second spectrum, $\chi_b$, consisting of a single Ru-Ru shell was simulated using the same parameters while systematically varying one or more of the structural parameters. Subsequently demodulated spectra, $\Delta \chi$, were calculated:

$$\Delta \chi = \chi_a - \chi_b$$

For clarity, the simulated spectra are denoted $\chi$, while functions, used for fitting, are denoted $\phi$. The demodulated spectra $\Delta \chi$ were fitted using two fitting functions, denoted $\phi_a$ and $\phi_b$:

$$\Delta \chi = \phi_a - \phi_b$$

containing the variables $N_a$, $R_a$ and $\sigma^2_a$ and $N_b$, $R_b$ and $\sigma^2_b$ for $\phi_a$ and $\phi_b$, respectively. Function $\phi_b$ is subtracted from function $\phi_a$, to generate the fit of the demodulated spectrum $\Delta \chi$. Initially, the parameters of $\phi_a$ were set to the parameters of the simulated Ru-Ru shell $\chi_a$. In an experiment, the parameters of $\chi_a$ are obtained from fitting a spectrum of one of the sample’s states using a standard fitting approach. The parameters for $\phi_b$ were allowed to float. The amplitude reduction factor was set to 1. This fitting strategy is schematically depicted in Figure (2.1).

In this schematic representation, a metallic Ru particle forms a shell of ruthenium oxide upon excitation with an O$_2$ pulse, and is reduced to metallic Ru when the gas is changed to H$_2$. Thus, in the theoretical simulation, the demodulated spectrum contains the information on the change of the Ru-Ru scattering paths, and the appearance of a ruthenium oxide phase.

The influence of noise was assessed by addition of random noise to the simulated spectra in $k^0$-weighting. To compare the influence of noise, the S/N ratio of the spectra is expressed as the absolute value of the quotient of the noise-free signal and the maximum amplitude of the noise, $S/N = \text{abs}(\text{max}(\text{Signal})/\text{max}(\text{Noise}))$. Since the signal is damped at higher $k$-values, the S/N also decreases at higher $k$. For comparison, the S/N ratio is expressed here as the maximum
S/N between \( k = 10 - 11 \) Å in \( k^0 \) weighting. The S/N ratio of experimental spectra can be compared to these simulated spectra to get a quantitative estimate of what precision on the structural parameters is possible.

To investigate the detection of minority species, additional spectra were simulated, being the sum of two species; a dominant metallic Ru particle (characterized by a Ru-Ru shell) and a minority ruthenium oxide species (characterized by a Ru-O shell). This could be representative of a Ru catalyst that is partially surface oxidized. The demodulated spectra can be expressed accordingly:

\[
\Delta \chi = \chi_{a,Ru-Ru} - (\chi_{b,Ru-Ru} + \chi_{b,Ru-O})
\]  

To investigate the detection limit for the Ru-O scattering shell as a function of the S/N ratio, \( \chi_{a,Ru-Ru} \) and \( \chi_{b,Ru-Ru} \) were kept fixed, while the coordination number of the Ru-O shell was varied from 0.06 to 1.2 (\( R_{b,Ru-O} \) and \( \sigma^2_{b,Ru-O} \) were kept fixed at 1.9279 Å and 0.003 Å² respectively) and the amplitude of the artificial noise added to the spectra was varied. The demodulated spectrum thus contains contributions from the Ru-O shell and the Ru-Ru shell, since it is assumed here that the oxide phase grows at the expense of the metallic phase.

For all fits of the simulated spectra, a \( k^1 \)-weighting and a \( k \)-range for the Fourier transformation...
of 2-14 Å\(^{-1}\) were used. The single shell demodulated spectra (equation 2.2) were fitted in R-space over a range between 1 and 3 Å. The two-shell demodulated spectra (equation 2.4) were fitted in two steps: first the Ru-Ru shell of the partially oxidized spectrum (\(\phi_{b,Ru-Ru}\)) was fitted over a R-range from 1.8 to 3 Å, while the values for the fully reduced Ru particle (\(\phi_{a,Ru-Ru}\)) were fixed to the values of the simulation. In an experiment \(\phi_{a,Ru-Ru}\) would be set to the structural parameters obtained from fitting the spectrum of the initial state fully reduced Ru particles using a standard fitting approach. In a second step, the values for \(\phi_{b,Ru-Ru}\) were fixed to the best-fit values, and the Ru-O shell was fitted with one fitting function \(\phi_{b,Ru-O}\) over a R-range from 1 to 3 Å, since the Ru-O shell is assumed to exist only in the spectrum \(\chi_b\) of the partially oxidized Ru particle.

The accuracy of a fitting parameter relates to the difference between the fit result and the original parameter of the simulated spectrum. As a measure for the precision of fit values, the uncertainty values as calculated by IFEFFIT were used. The precise fitting of the demodulated spectrum, is limited by two factors: the data quality, i.e. the S/N ratio in the spectrum \(\Delta\chi\), and the accuracy of the parameters of the initial fitting function, \(\phi_a\). To deconvolute these two error sources, two types of analysis were performed:

First, the fitting accuracy and precision of \(\Delta\chi\) was tested for different S/N ratios, while the parameters of \(\phi_a\) were assumed to be known. Second, the sensitivity of \(\Delta\chi\) to errors in parameters of \(\phi_a\) was tested by systematically varying the values of the parameters \(N_a\), \(R_a\), \(\sigma_a^2\) and \(\Delta E_0\) and mapping the fit result for \(N_b\), \(R_b\) and \(\sigma_b^2\).
2.4 Experimental approach

To test the proposed fitting approach, a modulated excitation oxidation / reduction experiment was performed on a real catalyst, which is analogous to our simulated system; an Al₂O₃ supported 2 wt-% Ru catalyst with a particle size between 10 nm and 30 nm (determined by scanning transmission electron microscopy) that is periodically reduced and partially oxidized. The catalyst was filled into a quartz capillary reactor (inner diameter 2.8 mm), which was heated from below by an air blower. The temperature in the reactor was \( \sim 265 \, ^\circ\text{C} \), the pressure in the reactor was kept at 1.5 bar absolute pressure. The catalyst was periodically oxidized and reduced with defined pulses of 0.73 \( \mu\text{-mol} \) H\(_2\) and 0.08 \( \mu\text{-mol} \) O\(_2\) in intervals of 80 s. Between the pulses, the lines and the reactor were flushed with Ar. The total length of a single cycle, consisting of one H\(_2\) and one O\(_2\) pulse, was 160 s. The cycle was repeated seven times.

Prior to the modulation experiment, the catalyst was heated under Ar atmosphere and reduced with 5% H\(_2\) in He for several minutes until the XAS spectra showed that the catalyst was fully reduced. During the modulation experiment, quick X-ray absorption spectra (QuickXAS) were collected at the SuperXAS beamline of the Swiss Light Source (SLS), Paul Scherrer Institut, Villigen, Switzerland. Spectra were collected at the ruthenium K-edge (22117 eV) in transmission mode in the middle of the catalyst bed. The Si(311) crystal of the QuickXAS monochromator oscillated at 1 Hz frequency, resulting in a time resolution of one spectrum per second (only the spectra in the direction of increasing energy were used). The QuickXAS data was treated with a Matlab script, where multiple modulation periods were averaged into one period, yielding one dataset with the absorption coefficient as a function of energy and time for a single period \( (A(E,t)) \). Based on this dataset, the demodulated dataset, \( A_k^\phi \), was calculated with a discrete formulation of equation (2.1).

The full QuickXAS spectra and the demodulated spectra were background subtracted and analyzed using the IFEFFIT software package. The QuickXAS spectra were analyzed using a standard fitting approach by minimizing the difference between the experimental data and the model. All fits (full spectra and demodulated spectra) of experimental spectra were done in R-space with a \( k^2 \)-weighting, over a \( k \)-range of 3-14 Å\(^{-1}\). The amplitude reduction factor was set to 0.85, as determined by fitting the spectra of a Ru foil. The full spectra were fitted with the metallic Ru-Ru structure with four free parameters \( (N, R, \sigma^2 \text{ and } \Delta E_0) \) over a range in R-space from 1.6 Å to 2.8 Å (uncorrected for phase shift).

The demodulated spectrum was fitted with the fit approach described above (see Figure (2.1)). The data were represented by two functions which are subtracted from each other (equation (2.3)). The first function was represented by the parameters of the original state, in this case the reduced state. The second function was represented by free floating structural parameters and represents the unknown state (i.e. the partially oxidized state). Since it is assumed that the reduced state only consists of a metallic Ru\(^0\) structure, the Ru-O shell of the ruthenium
2.4. EXPERIMENTAL APPROACH

oxide phase was only fitted for the partially oxidized state. Therefore the demodulated spectrum can be fitted with the difference of the fitting functions of the reduced state and the partially oxidized state:

\[ \chi_{\text{demodulated}} = \phi_{\text{reduced}} - \phi_{\text{oxidized}} = \phi(Ru - Ru)_{\text{reduced}} - (\phi(Ru - Ru) + \phi(Ru - O))_{\text{oxidized}} \] (2.5)

First, the metallic Ru-Ru shell of the pure metallic Ru phase was fitted with four free parameters (N, R, \(\sigma^2\) and \(\Delta E_0\)) over a range in R-space from 1.6 - 2.8 Å, which covers only the Ru-Ru shell. In a next step, those parameters were fixed to the best fit values, and the Ru-O and Ru-Ru shells of the RuO\(_2\) phase \[81\] were fitted over a larger range in R-space (1.1 - 2.8 Å). The value for \(\Delta E_0\) determined in the previous step was used, and the parameters for coordination number, bond distance and pseudo Debye-Waller factor were left floating free.

Finally, the experimental demodulated spectra need to be scaled correctly because the amplitude of the demodulated spectra depends on the shape of the excitation function. Urakawa et al. showed analytically that the ratio of the system response \(A(E)\) in phase domain (cf. equation (2.1)) upon a square wave excitation \(A(E)_{\text{sq}}\) and the response upon a sine wave excitation \(A(E)_{\text{sin}}\) is \(4/\pi\). \[83\]

Over the phase angle, the demodulated spectra go through negative and positive values. Thus the maximum absolute amplitude of a single demodulated spectrum is \(0.5 \times (4/\pi)\) times that of the difference spectrum. Practically, this can for instance be done by setting the edge step value of the demodulated spectrum to \(2/\pi \times\) that of the full spectra, which was here 0.175. The parameters for the edge position and background function of the demodulated spectrum were identical to the parameters of the full spectra. Only demodulated spectra at the fundamental frequency (\(k=1\) in equation (2.1)) are considered in this work. In an experiment with two distinct states, higher harmonics will show the same information, with a reduced amplitude. \[83\]
2.5 Results

2.5.1 Qualitative changes of demodulated spectra

The demodulation procedure yields a set of spectra, which contain all changes in the spectra upon the external stimulation. In a first step, the demodulated spectra can be interpreted qualitatively, to assess which of the structural parameters changed. Figure (2.2) shows the demodulated spectra originating from changes in a single structural parameter, such as N, R and $\sigma^2$.

Figure 2.2: Simulated full spectra (dashed line, left scale) and demodulated/difference spectra (solid lines, right scale) in A) k-space ($k^1$-weighting) and B) R-space (real part) where: top: only N changed (5%, 10%, 20%), middle: only $\sigma^2$ changed (0.0001 Å$^2$, 0.0005 Å$^2$, 0.001 Å$^2$), bottom: only R changed (0.001 Å, 0.005 Å, 0.01 Å, 0.02 Å).

Changes in the coordination number, N, lead to demodulated spectra that are in-phase with the original full spectra in k-space. The amplitude of the demodulated spectra linearly depends on the difference in N, since N appears in the EXAFS equation (eqn (2.1)) as a linear term. Therefore a demodulated spectrum which contains a change of 10% in N has 10% of the amplitude of
the original, full spectrum over the whole k-range. Changes in the Debye Waller factor, $\sigma^2$, lead to demodulated spectra that have the same frequency as the original spectrum, but are shifted slightly to lower k-values. Since $\sigma^2$ appears in the EXAFS equation as an exponential term, the change in amplitude due to a change in $\sigma^2$ does not scale linearly with the original spectrum over the whole k-range. Changes in $\sigma^2$ appear in the Fourier-transformed spectra (R-space) which are shifted by a constant phase shift with respect to the full spectrum (Figure (2.2b)). Demodulated spectra containing a change in bond distance, $R$, are phase-shifted with respect to the original spectrum. The Fourier-transformed demodulated spectra (Figure (2.2b)) are also shifted in phase. The phase shift depends on the magnitude of the change in R. Visual inspection of the experimental demodulated spectra as shown here, and comparison of these demodulated spectra to the full spectra provides a qualitative insight into which parameter changed in a modulation excitation experiment.

### 2.5.2 Fitting of noise-free demodulated spectra

Simulated noise-free demodulated spectra were created and fitted with the assumption that one spectrum $\chi_a$, represented by the fitting function $\phi_a$, is exactly known. The demodulated spectrum $\Delta \chi$, created by subtraction of $\chi_b$ from $\chi_a$, represents a difference in the structural parameters $N$, $R$ and $\sigma^2$ between $\chi_a$ and $\chi_b$. To fit the demodulated spectrum, the procedure outlined above and shown in Figure (2.1) was used, i.e. the demodulated spectrum, $\Delta \chi$, was fitted using two fitting functions $\phi_a$ and $\phi_b$, where the parameters of the first function $\phi_a$ were fixed to the parameters of the spectrum of the Ru metal, $\chi_a$, ($N_a = 12, R_a = 2.6657 \ \text{Å}$ and $\sigma^2_a = 0.003 \ \text{Å}^2$) and the parameters of the $\chi_b$ function were left free. Figure 2.3 shows the corresponding fit, perfectly matching the simulated spectrum. The fit is independent of the amplitude of the demodulated spectrum, so that even extremely small differences can be resolved in the absence of noise.

![Figure 2.3](image)

**Figure 2.3:** Simulated, $k^0$-weighted demodulated EXAFS spectrum (solid line) and fit (circles) with $N_a = 12, R_a = 2.6657 \ \text{Å}, \sigma^2_a = 0.003 \ \text{Å}^2, N_b = 11.4, R_b = 2.6667 \ \text{Å}, \sigma^2_b = 0.0031 \ \text{Å}^2$
2.5.3 Sensitivity to noise

To mimic a more realistic situation, the influence of noise on the fit of demodulated spectra was investigated. For visualization of the different tested noise levels, a simulated full spectrum is shown in Figure (2.4) with four different S/N ratios of 3.1, 6.3, 15.7 and 63.

Figure 2.4: Simulated \( k^1 \)-weighted full EXAFS spectra for the first metallic Ru-Ru shell at different S/N ratios (from top to bottom: 63, 15.7, 6.3, 3.1). The spectra were offset by 0.5 for clarity

To fit the demodulated spectra with different S/N ratios, the parameters of the first function \( \phi_a \) were again set to the parameters of the spectrum of the Ru metal, and all parameters of the \( \phi_b \) function were left free in the fits. The influence of noise on the accuracy of the fitting approach was tested by systematically varying each individual parameter of the second simulated spectrum, \( \chi_b \) to deconvolute the influence of changes in \( N_b, R_b \) and \( \sigma_b^2 \). The coordination number \( N_b \) was varied from 11.4 to 9.6, corresponding to changes in the coordination ranging between 5% and 20%. The bond distance \( R_b \) varied from 2.6707 Å to 2.7157 , corresponding to changes between 0.005 Å and 0.05 Å. The pseudo Debye Waller factor \( \sigma_b^2 \) ranged from 0.0035 Å\(^2\) to 0.005 Å\(^2\). These variations led to difference spectra similar to those in Figure (2.2), but with different noise levels added.

Figure (2.5) shows the resulting fit values of \( \phi_b \) plotted against the simulated values of \( \chi_b \) for different noise levels. Note that all parameters of \( \phi_b \) (\( N_b, R_b \) and \( \sigma_b^2 \)) were left floating during the fits.

The ideal result, where the fit value equals the simulation value is indicated by a dashed line. Lower noise levels (i.e. higher S/N ratio) allow better fits of small structural differences in terms of accuracy (deviation from the actual value) and precision, depicted by the error bars. This is expected, as the fit quality is governed by the S/N ratio of the demodulated spectrum. A small difference in any parameter leads to a small amplitude of the demodulated spectrum, and therefore to a lower S/N ratio in the demodulated spectrum. Experimentally, the S/N ratio can be increased by repeating the excitation period multiple times and averaging, or by optimizing
2.5. RESULTS

Figure 2.5: Fit results from fitting the demodulated spectrum with changes in \(N_b\) (A), \(\sigma^2_b\) (B) and \(R_b\) (C) for different signal-to-noise ratios; the black dotted line depicts the ideal values where the fit values equal the simulated values. The values for different signal-to-noise ratios are vertically offset for clarity, as indicated by the arrows. In all cases, all parameters (\(N_b\), \(\sigma^2_b\) and \(R_b\)) were allowed to float, while for clarity only the resulting fit parameter is shown, which was changed in the simulated data.

Furthermore, Figure 2.5 shows that small differences in the coordination number \(N\) of 1 \% can be resolved for a S/N ratio of 63 with a precision of ± 0.2 \% while larger differences (10 \%) can be fit well with S/N ratios of 6.3 with a precision of ± 1.8 \%. At an even lower S/N ratio of 3.1, 20 \% difference in \(N\) can be detected with a precision of ± 2.2 \%. A difference in the pseudo Debye Waller factor \(\sigma^2\) of 0.001 Å\(^2\) can not be resolved at a S/N ratio of 3.1. With a S/N ratio of 63, a difference in \(\sigma^2\) of 0.0005 Å\(^2\) can be accurately fitted and a precision of ± 2 × 10\(^{-5}\) Å\(^2\) was obtained. A shift in distance of 0.005 Å can be resolved from the fit with a good accuracy for a S/N ratio of the full spectra of 6.3 (result: 2.6709 Å ± 0.7 × 10\(^{-3}\) Å), while for a high S/N ratio of 63, even a shift in distance of 0.001 Å can be accurately fitted with a precision of ± 1.3 × 10\(^{-4}\) Å. Accordingly, fitting of demodulated spectra allows to resolve sub pico-meter bond length changes, provided that the spectra have a good S/N ratio. When all parameters of \(\chi_b\) (\(N_b\), \(R_b\) and \(\sigma^2_b\)) were varied simultaneously, the accuracy and precision on the individual structural parameters remained largely the same. Accordingly, we conclude that demodulated spectra, which contain a change in several structural parameters at the same time, can be used to fit the state of the second spectrum \(\chi_b\) with a precision well beyond that
set values for $\phi_a$ & fitted values for $\phi_b$ & difference $\phi_b - \phi_a$
\hline
$N_a$ & $\sigma_a^2$ [Å$^2$] & $R_a$ [Å] & $\Delta E_0$ [eV] & $N_b$ & $\sigma_b^2$ [Å$^2$] & $R_b$ [Å] & $\Delta N$ & $\Delta \sigma^2$ [Å$^2$] & $\Delta R$ [Å]
\hline
12 & 0.003 & 2.6657 & 0 & 12.07 & 0.00302 & 2.6707 & 0.07 & $2 \times 10^{-5}$ & 0.005
11.4 & 0.003 & 2.6657 & 0 & 11.47 & 0.00302 & 2.6710 & 0.07 & $2 \times 10^{-5}$ & 0.0053
12 & 0.0035 & 2.6657 & 0 & 12.07 & 0.00352 & 2.6712 & 0.07 & $2 \times 10^{-5}$ & 0.0055
12 & 0.003 & 2.6757 & 0 & 12.05 & 0.00302 & 2.6707 & 0.05 & $-9 \times 10^{-5}$ & 0.0048
12 & 0.003 & 2.6675 & 1 & 11.99 & 0.00302 & 2.6707 & -0.07 & $2 \times 10^{-5}$ & 0.005
\hline
Table 2.1: Effect of errors in parameters of the first function, $\phi_a$, (indicated in bold) on fitting of $\phi_b$; a difference spectrum was fitted that contains only a change in $R$ by $0.005$ Å ($N_a = N_b = 12$, $R_a = 2.6657$ Å, $R_b = 2.6707$ Å, $\sigma_a^2 = \sigma_b^2 = 0.003$ Å$^2$), S/N ratio 15.7. Fitting uncertainties are in $N_b < 1\%$, $R_b < 3 \times 10^{-4}$ Å, $\sigma_b^2 < 5 \times 10^{-5}$ Å$^2$.

2.5.4 Influence of fitting inaccuracy of the initial state

The proposed fit procedure of difference spectra involves fitting of the initial spectrum, $\chi_a$, as a first step to fitting the demodulated spectrum. Therefore the accuracy of the fit of the demodulated spectra depends directly on the accuracy of the fitted parameters of the initial spectrum, $N_a$, $R_a$, and $\sigma_a^2$. The accuracy obtained for these structural parameters equals that of the traditional fitting procedure used to fit the initial state. To determine to what extent these inaccuracies of the structural parameters of the initial spectrum affect the analysis, demodulated spectra $\Delta \chi$ were fitted with values for the parameters of $\phi_a$, which differ from those of $\chi_a$. $\Delta \chi$ was then fitted with freely floating $N_b$, $R_b$, and $\sigma_b^2$ for $\phi_b$. This procedure simulates the experimental case where the values of the initial state, derived from regular EXAFS fitting, are not accurately known.

Table 2.1 shows the fit results for the demodulated spectrum $\Delta \chi$ with a S/N ratio of the full spectra of 15.7. The values of $\phi_a$ were varied one by one. $N_a$ was decreased by 10%, $\sigma_a^2$ was increased by 0.0005 Å$^2$, $R_a$ was increased by 0.01 Å and $\Delta E_0$ was increased by 1 eV. The resulting values $N_b$, $\sigma_b^2$ and $R_b$ mostly compensated the variations in $N_a$, $\sigma_a^2$ and $R_a$ by a similar change. When $N_a$ was underestimated (11.4 instead of 12), the resulting $N_b$ was underestimated by the same amount (11.47 instead of 12.07). When $\sigma_a^2$ was increased by 0.005 Å$^2$, the resulting value for $\sigma_b^2$ also increased by 0.005 Å$^2$. An increase in $R_a$ by 0.01 Å led to an increase of $R_b$ by 0.009 Å. An error in $\Delta E_0$ by 1 eV was reflected by a slight decrease in $N_b$ by 0.08. In conclusion, the simulations showed that the difference between initial and final state, which is included in the demodulated spectra, can be accurately determined, even in case the initial state is not precisely known. Comparable results were obtained when all parameters of $\phi_a$ were changed simultaneously.
2.5. RESULTS

2.5.5 Detection of minority species

Minority species can be defined as those contributions to the XAS spectrum which have small amplitude, as compared to the major contribution. This can be for instance a surface phase which is different from the bulk, such as the surface oxide phase on the metallic core depicted in Figure (2.1). Since XAS averages over all atoms in the beam path, detection of such minority species is challenging. The detection limit for minority species mostly depends on the S/N ratio of the XAS spectra. Since the demodulation procedure removes the static species (e.g. the bulk) and noise, thereby improving the S/N ratio, it is also expected to increase sensitivity towards the detection of minority species, given that the majority and minority species can be separated in R-space. It is important to note that the modulated excitation technique will only detect those minority species that are formed reproducibly upon the excitation.

To describe a system where a Ru particle modulated between a fully reduced and a partially oxidized species, a minor contribution of an oxide phase was added to $\chi_b$ (Equation 2.4). Here, this surface oxide is represented only by a Ru-O scattering shell at 1.9279 Å. The fitting of the demodulated spectrum was done using Equation 2.4 where one state is represented by a Ru-Ru shell, and the second state, which includes the Ru-O minority species, is expressed as the sum of a Ru-Ru and a Ru-O shell. Prior to fitting of the minority Ru-O species, the Ru-Ru species of the difference spectrum was fitted over a narrow range in R-space, and its values fixed. It was found that for a high S/N ratio of 63, a minority Ru-O species can be detected with a coordination number as small as 0.06 with excellent precision ($N_{b,Ru-O} = 0.06 \pm 0.001$, $R_{b,Ru-O} = 1.924 \pm 0.009 \text{ Å}$, $\sigma^2_{b,Ru-O} = 0.003 \pm 0.003 \text{ Å}^2$), as shown in Figure (2.6).

![Simulated, $k^0$-weighted demodulated spectrum (empty circles) containing a minority Ru-O species ($N_{Ru-O} = 0.06$) with a S/N ratio of 63, fit (dashed line) and Ru-O fitting shell (solid line)](image)

Figure 2.6: Simulated, $k^0$-weighted demodulated spectrum (empty circles) containing a minority Ru-O species ($N_{Ru-O} = 0.06$) with a S/N ratio of 63, fit (dashed line) and Ru-O fitting shell (solid line)

This corresponds to an average of 1% of the sample being in the ruthenium oxide phase ($N_{Ru-O}$...
CHAPTER 2. MODULATED EXCITATION XAS

= 6 for the bulk RuO$_2$ phase). With a low S/N ratio of 6.4, even a Ru-O species with a coordination number of 1.2 could not be fitted with reasonable fit results. It can be concluded that the sensitivity to minority species depends strongly on the S/N ratio, so that a species with 1% concentration or less (compared to bulk) can be detected, provided that the data quality is sufficiently good. This is generally not possible with standard EXAFS analysis.

2.5.6 EXAFS fitting of experimental data

To verify the validity of the proposed fitting approach for experimental demodulated spectra, QuickXAS spectra of a supported Ru catalyst were collected during a modulated oxidation-reduction experiment and fitted. The normalized spectra of two full spectra, representing the catalyst after the H$_2$ pulse and after the O$_2$ pulse, their difference spectrum, and selected demodulated spectra for $\Phi^{PSD}_k$ from 30 - 360° are shown in Figure 2.7.

![Figure 2.7: Experimental Ru K-edge XAS spectra of a 2 wt-% Ru catalyst supported on Al$_2$O$_3$. Two selected, normalized XAS spectra are shown, after the H$_2$ pulse (red line) and the O$_2$ pulse (black line), respectively. The inset shows the temporal evolution of the absorption coefficient at 22134 eV, indicated by the vertical dashed line. Demodulated spectra for phase angles between 30° and 360° are shown along with the difference of the two full spectra (blue) for comparison. The selected demodulated spectrum at $\phi^{PSD}_k = 180°$ is indicated with a thick red line. The difference spectrum is offset by 0.05 for clarity.](image)

Both spectra are similar to metallic Ru, indicating that only a small amount of oxidation occurs upon O$_2$ pulsing. The evolution of the absorption coefficient above the whiteline (E = 22134 eV) for the averaged period is shown in the inset of Figure 2.7. This evolution is well reproducible over the seven periods that were used in this experiment. The lower values of the absorption
2.5. RESULTS

coefficient indicate the reduced state during the first 80 s, while the higher values during the last 80 s indicate the partially oxidized state. This stepwise signal indicates that the catalyst is in only two states, i.e. a fully reduced and partially oxidized state, while the transition between the states occurs within a few seconds.

While the difference spectrum of the two full spectra shows little structure, the demodulated spectra show a clear EXAFS like structure. In contrast to the difference spectra, the demodulated spectra have good data quality, which allows EXAFS fitting. Figure 2.8 shows the Fourier transformed EXAFS spectrum after the H\textsubscript{2} pulse at t = 40 s, after the O\textsubscript{2} pulse at t = 120 s and the Fourier transformed demodulated EXAFS spectrum at Φ\textsubscript{PSD} = 180°.

![Figure 2.8](image)

**Figure 2.8:** Fourier transform magnitude (in k\textsuperscript{2}-weighting) and imaginary part for the full spectra (top) after the H\textsubscript{2} pulse in the fully reduced state (red), after the O\textsubscript{2} pulse in the partially oxidized state (black) and the demodulated spectrum for Φ\textsubscript{PSD} = 180° (bottom) with the corresponding fit (dashed line). The resulting fit values of the full spectrum in the reduced state were used as input parameters for the fit of the demodulated spectrum, according to the fitting procedure described in the text. The spectra are not phase corrected.

In R-space, the Ru-Ru peak clearly dominates the full spectra, which makes fitting of the Ru-O minority shell in the full spectra very difficult, resulting in high uncertainties in the fit values. The Fourier transformed demodulated spectrum shows two contributions in R-space, the Ru-Ru peak at \sim 2.4 Å and the Ru-O peak at \sim 1.5 Å (not corrected for phase shifts). Following the analysis procedure described in Figure 2.1, the full EXAFS spectrum representing the catalyst
in the reduced state was fitted first. Subsequently the demodulated spectrum at $\Phi_{PSD}^k = 180^\circ$ was fitted. This specific phase angle was chosen because it has the highest amplitude of the demodulated spectra (therefore the best S/N ratio), see Figure 2.7. The resulting fits are shown in Figure 2.8.

The fit of the demodulated spectrum shows that partial oxidation leads to a decrease in $N_{\text{Ru-Ru}}$ by $0.8 \pm 0.2$, a small increase in $R_{\text{Ru-Ru}}$ of $0.0022 \pm 0.0006$ Å and a decrease in $\sigma^2_{\text{Ru-Ru}}$ by $1 \times 10^{-4} \pm 1 \times 10^{-4}$ Å². This is in good agreement with the differences found in the fits of the full spectra, while the precision (given by the Ifffit software package) is much better when fitting the demodulated spectrum. Compared to the fitted coordination number of the full EXAFS spectrum ($10 \pm 1.2$), fitting of the demodulated spectrum allows determination of minute changes in the Ru-Ru coordination number with a precision of 2 %.

The Ru-O shell of the demodulated spectrum was fitted with an average coordination number of $0.25 \pm 0.09$, a bond distance of $1.945 \pm 0.016$ Å and a pseudo Debye-Waller factor $\sigma^2_{\text{Ru-O}}$ of $0.0035 \pm 0.0035$ Å². For comparison, the Ru-O shell of a bulk ruthenium oxide structure has a coordination number of 6 at a distance of 1.928 Å. [81] This suggests that the O₂ pulse during the experiment creates a thin layer of ruthenium oxide on top of the Ru particles with a Ru-O bond distance which is higher than in bulk ruthenium oxide.
2.6 DISCUSSION

2.6 Discussion

2.6.1 Improved precision and sensitivity of XAS by using the modulated excitation technique

The presented simulated and experimental demodulated spectra showed that quantitative detection of small structural changes in demodulated spectra is possible with high precision. \[68\] \[69\] While the concept can be similarly applied to difference spectra, the focus was put here on demodulated spectra, since they contain all differences in the spectra that occur upon excitation. In addition, the demodulated spectra contain all changes that occur as a result of the excitation, and not just the change between two selected states. To exploit the improved accuracy and precision of demodulated spectra, a robust fitting approach was developed.

The application of the demodulation procedure to a modulated excitation EXAFS spectra dataset leads to an improved S/N ratio of the demodulated spectra in comparison to difference spectra, because the demodulation procedure filters the EXAFS data with the frequency of the applied external stimulation and thereby removes contributions of spectator species and noise. The S/N ratio is therefore the only factor limiting the smallest structural difference that can be resolved. Based on the simulations, it can be estimated that for high quality spectra, changes in coordination number better than 1% and changes in bond distance below 0.001 Å can be detected and quantified using the proposed fitting strategy, with a precision (i.e. fit uncertainty) of 0.2 % and 1 × 10^{-4} Å respectively. Fitting the demodulated spectrum derived from the experimental data set with a not very favorable S/N ratio in the original QuickXAS spectra (the difference signal has little structure) yields a precision of \(\sim 2 \%\) for the change in coordination number, 6 × 10^{-4} Å for the change in radial distance and 1 × 10^{-4} Å\(^2\) for the change in pseudo Debye Waller factor. This precision, which is high compared to standard fitting of full EXAFS spectra, is obtained by fitting only those features in the spectra that change (i.e. the demodulated spectra), using the proposed fitting approach. Although the size of the Ru particles is rather large, the demodulation technique still allows identification and fitting of the active species (i.e. those atoms that react to the excitation). This is because contributions of the spectator species (the non-reactive parts of the sample) to the spectra, and noise, are filtered out by the demodulation procedure. The results from the simulations indicate that these values can be decreased even further, if the S/N ratio of the demodulated spectra is improved, e.g. by simply increasing the number of modulation periods.

Even if the original state of the sample is not known precisely, and there are large uncertainties in the fit of the initial spectrum, the relative changes in the state of the active sites can be quantified very precisely. Note that the active site is defined in this context as any atom (of which the absorption edge is studied) of the sample that reacts to the external excitation. The experimental data, where a Ru catalyst was periodically reduced and partially oxidized, corroborate the validity of the proposed fitting approach. Furthermore, application of the proposed quantitative
analysis for demodulated spectra on the experimental data allows detection of small changes in the catalyst’s structure, which is not possible with standard EXAFS analysis. This is due to the removal of spectator species from the spectra. For optimized conditions (higher sample concentration, repeating the sequence more often, smaller particle size), the detection limit can be even lower, since the detection limit essentially depends on the S/N ratio.

### 2.6.2 Sensitive detection of intermediate minority species

Minority species, defined in this context as those species that have a small contribution to the spectrum, compared to the main contribution, can be detected with high sensitivity, due to the removal of noise and spectator species by the demodulation procedure and the averaging of multiple modulation periods. The demodulated spectra are calculated from the whole dataset, and therefore contain all spectral variations upon the excitation. Compared to employing difference spectra of initial and final state, this has several benefits. The difference spectrum requires picking two spectra from which the difference is calculated. In the presented case with two discrete states, this is relatively straightforward and the S/N ratio of the difference spectrum could be improved by simply averaging several full spectra of each state. In a more complex experiment, with slow changes or intermediate states (for instance oxidation proceeding through intermediate oxide phases) it is difficult to estimate which spectra to choose for calculation of a difference spectrum, and averaging of several spectra may smooth out intermediate states. In contrast, the demodulated spectra include all spectral differences at high S/N ratio (due to the removal of noise and spectator species) at different phase angles without the need to calculate differences from full spectra at an estimated time.

Demodulated spectra of intermediate states can be analyzed with the same procedure as developed above, and their analysis ultimately profits from the improved detection limit and precision. This is the strength of the modulated excitation XAS technique, which basically generates high quality difference spectra for the entire modulation period, including intermediate states, which can be analyzed quantitatively with our fitting approach. The detection of minority intermediate states is not possible using steady-state experiments, where multiple spectra before and after the sample’s excitation are averaged for improved S/N ratio.

### 2.6.3 Possible applications

All experiments in which reversible structural changes of a sample can be induced will benefit from the application of modulated-excitation XAS in combination with the quantitative analysis method presented here. This includes for instance electrochemistry experiments, where either the voltage applied to an electrode, or the gas composition in a fuel cell is varied periodically, leading to small changes in the electrode’s structure or surface coverage. Periodic modulations of magnetization direction or pressure can also be used for modulation...
spectroscopy experiments in combination with the presented quantitative analysis of EXAFS spectra. Application of the modulated excitation technique to pump-probe experiments, where a particle is periodically excited by laser radiation and the state of the particle is probed with XAS \cite{69} can improve data quality by removing static parts and noise from the spectrum. Other examples include heterogeneous catalysis experiments, where the varying gas atmosphere around a catalyst or its temperature and pressure lead to small changes in its structure. \cite{86,87} Since EXAFS is usually not considered to be a surface sensitive technique, analysis of particles with a low surface to volume ratio, such as large catalyst particles, could especially profit from the application of modulated excitation EXAFS. The requirement for a modulated excitation experiment is reproducibility of excitation, which usually presents no problem with an automated, computer controlled experimental setup. Additionally, the induced structural changes need to be reversible.
2.7 Conclusion

The modulated excitation technique applied to XAS is a powerful method to extract quantitative information of structural changes which occur due to modulated excitation of the system, with improved precision. We have developed a robust analysis approach for fitting the demodulated spectra that is conceptually similar to the fitting of difference spectra. By filtering of the XAS spectra with the excitation frequency and averaging of multiple modulation periods, the S/N ratio is improved significantly and consequently small changes in structural parameters under changing reaction conditions can be extracted. Compared to standard EXAFS analysis, the fit precision of demodulated spectra is improved by a factor of more than 5. Thus XAS becomes sensitive to minute changes in the sample’s structure. In addition to the improved precision, modulated excitation XAS also allows detecting minority species with high sensitivity. This was demonstrated with experimental data of periodic reduction and oxidation of a supported Ru catalyst, where a minor oxide species was detected by analysis of a demodulated spectrum, which was not detectable using the regular analysis of the full or difference EXAFS spectra.

Modulated excitation XAS extends the capabilities of EXAFS (element selectivity, possibility to measure under realistic conditions, no requirement for crystalline samples) to decipher changes in the structure of the active sites with increased sensitivity and precision. It can therefore be expected that modulated excitation XAS will be widely applied to systems which react reversibly to an external stimulation. The technique is ideally suited to study materials which are routinely exposed to varying conditions, such as those reactions in the following chapters.
Chapter 3

High temperature H$_2$S removal over manganese based sorbents

3.1 Abstract

Cleaning of producer gas from biomass gasification is required for further processing, e.g. to avoid catalyst poisoning in subsequent conversion steps or corrosion. High-temperature gas cleaning, of which sulfur removal is an important part, is a promising way to improve the overall efficiency of biomass conversion. In a high temperature chemical looping desulfurization process H$_2$S, which is the main sulfur species in biomass-derived producer gas, is removed by a sorbent. This sorbent material, here manganese oxide, is cycled between producer gas from the gasifier to remove sulfur species, and an oxidizing atmosphere, in which the sulfur species are released as SO$_2$. Alternatively, the use of such material as reactive bed material could be integrated into an allothermal dual fluidized bed gasifier, where heat is transported to the fuel via a solid bed material. To mimic such processes, manganese-based materials were subjected to a periodically changing gas atmosphere in a laboratory reactor. The fuel reactor gas contained H$_2$, CO, CH$_4$ and H$_2$S, similar as in the producer gas, and the oxidizing reactor contained diluted O$_2$. Mass spectrometry showed that most of the H$_2$S is taken up by the sample in the fuel reactor part, while also some unwanted SO$_2$ is generated in the fuel reactor part. Most of the sulfur is released in the oxidizing reactor. Simultaneous in situ X-ray absorption spectroscopy (XAS) of the Mn materials during different stages of the chemical looping desulfurization process showed that the initial Mn$_3$O$_4$ is transformed in the presence of H$_2$S to MnS via a MnO intermediate in the fuel reactor. Oxygen from the reduction of Mn$_3$O$_4$ oxidizes some H$_2$S to the undesired SO$_2$ in the fuel reactor. Upon exposure to O$_2$, MnS is again oxidized to Mn$_3$O$_4$ via MnO, releasing SO$_2$. The presence of CO and/or CH$_4$ in the fuel reactor has no effect on this mechanism. Measuring the structure-performance relationship of gas cleaning materials with in situ methods will enable knowledge-based materials development for improved performance.
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The Hg-intrusion porosimetry measurements were performed by Donald Scharf at EMPA, the attrition resistant support was supplied by Naomie van Garderen and Frank Clemens at EMPA. The Mn/Mg – ZrO$_2$ sample was supplied by Martin Seemann at Chalmers University (Gothenburg, Sweden).
3.2 Introduction

As pointed out in chapter 1.1, biomass, such as wood, is a promising feedstock to replace fossil fuels with renewable, CO₂ neutral feedstocks. Gasification of the solid biomass generates producer gas (syngas), which is a mixture of mainly H₂, CO, CO₂, CH₄, C₂H₄ and H₂O, which is subsequently used for electricity production or chemical synthesis to produce synthetic fuels. Further, a number of undesired chemical species are also part of the gas matrix, such as tars, alkali metals, chlorine, nitrogen compounds and both, inorganic (H₂S, COS, CS₂) and organic (C₄H₄S, C₈H₆S...) sulfur species. These sulfur species are typically found in the concentration range of several tens to hundreds of ppm. Sulfur species are known catalyst poisons, and thus need to be removed to protect downstream catalysts. Typically, sulfur, along with other species, is removed by scrubbing of the gas stream at low temperatures. After low temperature scrubbing, the cleaned gas is reheated up to synthesis temperatures. Even though the heat can be partially recovered, the low temperature gas cleaning step is one of the major cost factors in the overall process. Therefore, high temperature gas cleaning, which operates between the gasification temperature (∼850 °C) and the synthesis temperature of subsequent catalytic conversion (e.g. ∼300 °C for methane synthesis), is desired.

In this chapter, a hot gas cleaning process to remove H₂S was investigated, which we call chemical looping desulfurization (CLD), and could generally be run downstream of gasification, or be integrated with allothermal dual fluidized bed gasification. In an allothermal gasifier, heat is supplied from the outside, i.e. not by partial combustion of the fuel directly in the gasifier. The heat can for instance be transported by a bed material, which could contain a sorbent material. In CLD a sorbent is exposed to the sulfur-laden gas, thereby specifically absorbing the sulfur species from the gas phase. After the sulfur storage capacity (i.e. the maximum amount of sulfur that can be taken up by the sorbent) is reached, the material needs to be regenerated, where the sulfur is removed from the sorption material.

The cyclic sulfidation - regeneration can for instance be implemented downstream of the gasification in a swing reactor design or a dual fluidized bed system where the sorbent is circulated between a zone where sulfur needs to be removed from the fuel and a regeneration zone, where sulfur is oxidized, similar to a chemical looping process. In consequence, the sorbent could alternatively be used as reactive bed material in allothermal dual fluidized bed gasification systems, such as the FICFB of TU Vienna or the Milena gasifier by the Energy research centre of the Netherlands (ECN). Previously, Mn based materials not only showed sulfur capture capacity, but also performed well with respect to tar reforming and oxygen transport from the combustion zone into the gasification zone. A dual fluidized bed scheme for CLD however requires a support material that is mechanically stable and attrition resistant, due to the mechanic stress of the fluidized particles. Such an attrition resistant support was developed earlier and used in this study.
Several protocols for regeneration of S laden materials have been tested, typically reduction, oxidation, steaming or desorption in inert gas. Extensive research has been performed on selection of materials for sulfur removal, of which the most studied materials are oxides of Zn, Zn-Ti, Fe, Cu and Mn, in various configurations, mixtures and with dopants. Important criteria for materials selection are price, the minimum achievable sulfur concentration in the cleaned gas, maximum sulfur sorption capacity and stability against attrition and performance degradation. Among the proposed systems, Mn-based materials are potential candidates due to their stability and good sulfur uptake capacity. Ben-Slimane and Hepworth conducted extensive studies on Mn-based sorbents for removal of \( \text{H}_2\text{S} \) from simulated producer gas at 950 °C and regeneration in air or diluted \( \text{O}_2 \). Based on thermodynamic considerations, they proposed a mechanism where \( \text{Mn}_3\text{O}_4 \) is quickly reduced by \( \text{H}_2 \) to \( \text{MnO} \), which then reacts with \( \text{H}_2\text{S} \) to form \( \text{MnS} \) and \( \text{H}_2\text{O} \). Recent experiments with Mn-based sorbents showed that close to 100% \( \text{H}_2\text{S} \) removal can be achieved at 700 °C over multiple cycles in simulated wet syngas, using oxidative regeneration with oxygen or steam. Mn-based sorbents were tested for more than 100 cycles of sulfidation and oxidative regeneration, and it was suggested that \( \text{HCl} \) and \( \text{HF} \) can be removed simultaneously. Coking is typically not a problem, because carbon deposits are removed in the oxidizing regeneration part of the reactor.

The mechanisms for sulfur removal and regeneration proposed were derived from thermodynamic considerations, gas analysis, gravimetry or ex situ measurements of the sorbent’s state, e.g. by X-ray diffraction (XRD) of the fresh and used samples. On the other hand, in situ studies, which probe the state of the sorption material during the reaction while the gas composition is measured, allow for a more direct observation of the mechanisms that occur during sulfur uptake and release. Among the available methods, X-ray absorption spectroscopy (XAS) is very powerful, because it yields element-specific information on the local geometric structure (type of nearest neighbors, bond distances, oxidation state and electronic structure) of the sorption material, and can be measured under reaction conditions (high temperatures and atmospheric pressure).

In this chapter, the structure-performance relationship of Mn-based sulfur sorption materials was studied during the CLD process with in situ XAS, while simultaneously measuring the gas composition with a mass spectrometer. This allowed to identify a general mechanism for sulfur transport over Mn-based sorbents.
3.3 Experimental approach

3.3.1 Materials

In this chapter, two Mn-based materials that have proven to be attrition resistant were compared. One sample was a powder of spherical, freeze-granulated Mn$_3$O$_4$/Mg–ZrO$_2$ particles (~90 µm diameter), $^{[110]}$ which will be called Mn-Zr throughout this chapter. This material showed previously good tar reforming properties in a chemical looping reactor with real biomass $^{[97,98]}$ and in lab scale experiments with model compounds. $^{[99,100]}$ The second sample was an Mn-impregnated support (9 wt-% Mn, determined by inductively coupled plasma optical emission spectroscopy, ICP-OES) based on porous diatomite, that is porous and attrition resistant, consisting mostly of Si, Al, O and some Fe, Ca and Mg. $^{[103]}$ This sample will be called Mn-D in the following. Impregnation of the diatomite support followed the protocol by Bakker et al, where the support was impregnated in an excess of Mn-acetate solution and was dried at 105 °C for 1h and calcined in static air for 6 h at 700 °C. $^{[106]}$ For the tested sample, the impregnation procedure was repeated five times to increase the Mn loading. The fresh samples were characterized by N$_2$ physisorption and Hg intrusion porosimetry. The most important properties of both samples are summarized in table (3.1).

<table>
<thead>
<tr>
<th></th>
<th>BET surface</th>
<th>Mn-loading</th>
<th>BJH micropores fraction</th>
<th>particle size and shape</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m$^2$ g$^{-1}$</td>
<td>wt-%</td>
<td>%</td>
<td>≤ 20 nm</td>
</tr>
<tr>
<td>MnZr</td>
<td>0.9</td>
<td>29</td>
<td>48</td>
<td>32</td>
</tr>
<tr>
<td>MnD</td>
<td>3.0</td>
<td>9</td>
<td>21</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 3.1: Characteristics of the tested samples.

The cumulative pore volume for the Mn-Zr sample, the Mn-D sample, and the blank diatomite based, derived from Hg porosimetry, is shown in Figure (3.1). The pore size distribution shows that the Mn-Zr sample has mostly macropores with a size between 300 and 400 nm. The Mn-D sample has macropores with a size around 1000 nm. Compared to the fresh diatomite based support before impregnation with Mn, the pore size is slightly reduced. The pore size distribution (see table 3.1), derived from N$_2$ physisorption, shows that the Mn-Zr sample has a larger fraction of micropores (< 20 nm), compared to the Mn-D sample. Of each sample, ~15 mg were put in the quartz capillary between plugs of quartz wool.
3.3.2 Experimental setup

The employed reactor consists of a quartz capillary with 2 mm outer diameter and 0.01 mm wall thickness (Hilgenberg) which was kept at an overpressure of 0.3 - 0.5 bar, and which was heated from below with a hot air blower (Leister). The capillaries were connected to steel tubes and sealed with polytetrafluoroethylene (PTFE) tape and o-rings. Gas analysis was performed with a Pfeiffer Omnistar mass spectrometer. The gas lines to and from the reactor were coated to minimize sulfur adsorption (Restek).

The temperature in the reactor was between 550 °C and 600 °C, measured with a thermocouple outside of the reactor. Measuring the temperature with a thermocouple inside the reactor had an influence on the measurements of sulfur species, and was therefore avoided. The samples were exposed to periodic cycles of gas composition, simulating conditions in a fuel reactor with and without sulfur, and subsequent exposure to a gas composition that simulates an oxidizing reactor. One such sequence is schematically shown in Figure (3.2).

The experimental conditions were varied according to table (3.2).

3.3.3 XAS setup

The in situ experiments at the Mn K-edge (6539 eV) were performed at the SuperXAS beamline at the Swiss Light Source, using a QuickXAS monochromator with a Si (111) channel-cut crystal that was oscillated at a frequency of 0.2 Hz, resulting in 2 spectra (in direction of increasing
3.3. EXPERIMENTAL APPROACH

Figure 3.2: Schematic sequence of gas flows during the in-situ XAS experiment

<table>
<thead>
<tr>
<th>sample</th>
<th>purge</th>
<th>reduction</th>
<th>fuel reactor</th>
<th>purge</th>
<th>oxidizing reactor</th>
<th>repetitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-Zr</td>
<td>Ar</td>
<td>1.25 % H₂</td>
<td>1.25 % H₂ + 0.25 %</td>
<td>Ar</td>
<td>1.25 % O₂</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25 % CO</td>
<td>CO + 1000 ppm H₂S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-D</td>
<td>Ar</td>
<td>1.25 % H₂</td>
<td>1.25 % H₂ + 1000 ppm</td>
<td>Ar</td>
<td>5 % O₂</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂S</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: Experimental conditions of the in situ experiments

The X-ray beam was focused to a spot of $\sim 100 \mu m$ in diameter by a Rh-coated toroidal mirror. Spectra were collected in fluorescence mode, using a passivated implanted planar silicon (PIPS) diode (Canberra) for the fluorescence signal and a He filled ion chamber for measuring the incoming beam intensity. For comparison, XAS spectra of reference materials ($\text{MnO}_2$, $\text{Mn}_2\text{O}_3$, $\text{Mn}_3\text{O}_4$, $\text{MnSO}_4 \times \text{H}_2\text{O}$, MnO, MnS and Mn metal foil) were acquired in transmission mode.

3.3.4 XAS data analysis

The raw data was processed with a Matlab script, which calibrates the energy and averages multiple repetitive cycles into one dataset of 120 spectra. Data reduction (background correction and normalization) and analysis of XAS spectra was performed with the IFEFFIT software suite. The X-ray beam was focused to a spot of $\sim 100 \mu m$ in diameter by a Rh-coated toroidal mirror. Spectra were collected in fluorescence mode, using a passivated implanted planar silicon (PIPS) diode (Canberra) for the fluorescence signal and a He filled ion chamber for measuring the incoming beam intensity. For comparison, XAS spectra of reference materials ($\text{MnO}_2$, $\text{Mn}_2\text{O}_3$, $\text{Mn}_3\text{O}_4$, $\text{MnSO}_4 \times \text{H}_2\text{O}$, MnO, MnS and Mn metal foil) were acquired in transmission mode.

3.3.4 XAS data analysis

The raw data was processed with a Matlab script, which calibrates the energy and averages multiple repetitive cycles into one dataset of 120 spectra. Data reduction (background correction and normalization) and analysis of XAS spectra was performed with the IFEFFIT software suite. The LCA was forced to sum the components to 100 % with each component having a weight between 0 and 100 % and all components were allowed to shift in energy, using the same $E_0$ energy) per 10 seconds. The X-ray beam was focused to a spot of $\sim 100 \mu m$ in diameter by a Rh-coated toroidal mirror. Spectra were collected in fluorescence mode, using a passivated implanted planar silicon (PIPS) diode (Canberra) for the fluorescence signal and a He filled ion chamber for measuring the incoming beam intensity. For comparison, XAS spectra of reference materials ($\text{MnO}_2$, $\text{Mn}_2\text{O}_3$, $\text{Mn}_3\text{O}_4$, $\text{MnSO}_4 \times \text{H}_2\text{O}$, MnO, MnS and Mn metal foil) were acquired in transmission mode.
Chapter 3. Desulfurization over MN

3.3.5 Thermodynamic calculations

Phase diagrams were calculated with the HSC 7.0 software. [112] The software allows calculating the phase diagrams for three elements, where two partial pressures or one partial pressure and the temperature need to be fixed. The thermodynamically favored phase is then plotted as a function of the two remaining parameters.
3.4 Results

To study the relation between reactivity of the Mn towards H₂S and the structure of Mn, in situ experiments were performed. Simultaneous measurement of the gas phase, by mass spectrometry, and of the structure, by XAS, allows correlating reactivity and structure. Figure 3.3 shows XAS spectra of reference Mn compounds, and selected XAS spectra of the Mn-Zr sample.

![Figure 3.3: a: selected in situ XAS spectra at the Mn K-edge of the Mn-Zr sample (with H₂, H₂S and CO in the fuel reactor part) b: normalized XAS spectra at the Mn K-edge of reference compounds.](image)

The reference spectra in Figure 3.3b show that the position of the absorption edge of the reference spectra shows a clear trend of the absorption edge to move to higher energies for higher oxidation states. The sample is reduced upon addition of H₂S at 200 s from Mn^{II,III} to Mn^{II}, which is indicated by the position of the absorption edge shifting to lower energies. At 200 s and 300 s, the sample’s spectrum shows the same characteristic shape as the Mn₃O₄ reference, indicating that the sample is not reduced in the presence of H₂ alone.

Selected mass spectrometry signals of the experiment with the Mn-Zr sample are shown at the reactor inlet (dashed lines) and outlet (solid lines) in Figure 3.4. No significant H₂ consumption is measured during the sulfur-free feed. Sulfur is consumed by the material as H₂S during the fuel reactor part and released as SO₂ during the oxidizing reactor part of the sequence. In addition to the observed drop of the H₂S signal between inlet and outlet, there is a small SO₂
CHAPTER 3. DESULFURIZATION OVER Mn

Figure 3.4: Mass spectrometry signals of m/z 34 (top) and m/z 64 (middle) for the inlet (dashed lines) and outlet (solid lines) of the reactor, and the corresponding composition of the Mn-Zr sample as derived from Linear Combination Analysis (LCA) of the XANES data (bottom). Note that the spectra were corrected for self-absorption before LCA.

signal at the outlet of the fuel reactor part, which is slowly decreasing over time. During the 540 s of H$_2$S in the feed gas, there is no change in the H$_2$S signal, indicating that the sulfur-uptake capacity is not reached. During the oxidizing part of the sequence, O$_2$ is consumed by the material, while SO$_2$ is generated.

To determine the state of the sample during the sulfur uptake and release, linear combination analysis (LCA) of the XAS spectra of Mn-Zr was performed with three reference compounds Mn$_3$O$_4$, MnO and MnS. Linear combination fits of the spectra that included MnSO$_4$ × H$_2$O resulted in no contribution of MnSO$_4$ × H$_2$O, and therefore it was not included in the LCA.

The resulting linear combination in Figure 3.4 shows that the Mn-Zr sample mostly consists of Mn$_3$O$_4$ (∼90%) and some MnS (<10%) at the beginning of the sequence. Note that the MnS contribution is likely to stem from sulfidation in the previous cycle. When H$_2$S is added, up to 55% of the sample is transformed to MnO at the expense of Mn$_3$O$_4$. After the MnO fraction reaches its maximum, MnO is transformed into MnS, which makes up the majority of the final composition (∼48%), while some Mn$_3$O$_4$ (∼29%) and MnO (∼23%) remain. Upon oxidation, the sample is quickly oxidized to Mn$_3$O$_4$ via an MnO intermediate.

The Mn-D sample shows similar reactivity and structural changes as the Mn-Zr sample. This is shown in Figure 3.5, where XAS and MS data from the experiment with 1.25 % H$_2$ and 1000 ppm H$_2$S in the reductive part and 5 % O$_2$ in the oxidative part are shown. The Mn$_3$O$_4$ phase,
3.4. RESULTS

Figure 3.5: Mass spectrometry signals of m/z 34 (top) and m/z 64 (middle) for the inlet (dashed lines) and outlet (solid lines) of the reactor, and the corresponding composition of the Mn-D sample as derived from Linear Combination Analysis (LCA) of the XANES data (bottom). Note that the spectra were corrected for self-absorption before LCA.

which is the dominant phase after oxidation, is reduced by H$_2$S to MnO, until ∼ 60% of the probed sample is in the MnO phase. Subsequently, MnO is transformed to MnS, while Mn$_3$O$_4$ is further reduced, until it is almost completely converted. During this process, the majority of H$_2$S is consumed, while some SO$_2$ is generated. SO$_2$ generation starts at the onset of the reduction of Mn$_3$O$_4$ and decreases over time during the fuel reactor sequence. Upon oxidation, MnS is quickly and fully oxidized to Mn$_3$O$_4$, inducing a pulse of SO$_2$. 
3.5 Discussion

Mass spectrometry was combined with XAS to probe the performance and the structure of the Mn-based materials. This allows proposing a general mechanism for sulfur transport over Mn-based materials. In the first step, $\text{Mn}_3\text{O}_4$ is reduced to MnO, while $\text{H}_2\text{S}$ is oxidized to $\text{SO}_2$ using oxygen that is released from $\text{Mn}_3\text{O}_4$. Subsequently, the oxygen in MnO is exchanged by sulfur, forming MnS and H$_2$O. In the net reaction, 10 moles $\text{H}_2\text{S}$ are consumed to form 9 moles of MnS and one mole $\text{SO}_2$. Under oxidizing conditions, sulfur in MnS is exchanged with O$_2$, forming MnO and $\text{SO}_2$. Subsequently, MnO is quickly further oxidized to $\text{Mn}_3\text{O}_4$.

Sulfidation in the fuel reactor:

\[
3 \text{Mn}_3\text{O}_4 + \text{H}_2\text{S} \rightarrow 9 \text{MnO} + \text{SO}_2 + \text{H}_2\text{O} \tag{3.1}
\]
\[
\text{MnO} + \text{H}_2\text{S} \rightarrow \text{MnS} + \text{H}_2\text{O} \tag{3.2}
\]

Net sulfidation reaction:

\[
3 \text{Mn}_3\text{O}_4 + 10 \text{H}_2\text{S} \rightarrow 9 \text{MnS} + \text{SO}_2 + 10 \text{H}_2\text{O} \tag{3.3}
\]

$\text{SO}_2$ release in the oxidizing reactor:

\[
2 \text{MnS} + 3 \text{O}_2 \rightarrow 2 \text{MnO} + 2 \text{SO}_2 \tag{3.4}
\]
\[
6 \text{MnO} + \text{O}_2 \rightarrow 2 \text{Mn}_3\text{O}_4 \tag{3.5}
\]

Net regeneration reaction:

\[
3 \text{MnS} + 5 \text{O}_2 \rightarrow \text{Mn}_3\text{O}_4 + 3 \text{SO}_2 \tag{3.6}
\]

For both samples, the same mechanism of reduction of $\text{Mn}_3\text{O}_4$ to MnS via MnO is observed. For the Mn-D sample, no remaining $\text{Mn}_3\text{O}_4$ was observed, while the Mn-Zr sample showed some remaining $\text{Mn}_3\text{O}_4$ that was not reduced to MnO. This indicates that Mn-D is used more efficiently for sulfidation.

In the LCA results in Figures (3.4) and (3.5), it can be seen that the Mn in the Mn-D sample reacts faster than in the Mn-Zr sample. The reduction of $\text{Mn}_3\text{O}_4$ to MnO upon exposure to H$_2$S (reaction (3.1)) proceeds significantly faster for the Mn-D sample than for the Mn-Zr sample. This could be explained by the differences in particle properties; the Mn-Zr sample has three times lower BET surface, and three times higher Mn loading, compared to the Mn-D sample (see table 3.1), leading to approximately nine times higher Mn loading per surface area. This could lead to slower bulk diffusion into the Mn of the Mn-Zr sample, explaining the differences in observed reaction rate of the Mn. In addition, the pores of the Mn-D sample are larger (see Figure 3.1), which would make gas transport in the Mn-D sample faster. It can be concluded that the porous structure of the diatomite based material is more favorable for chemical looping applications, where not only sulfur uptake capacity, but also the reaction rate is important for efficient reactor design.
In none of the experiments was it possible to reduce significant parts of Mn$_3$O$_4$ with H$_2$ alone, in the range of temperatures that were tested. However, upon exposure to H$_2$S, Mn$_3$O$_4$ is readily reduced to MnO, and then sulfided to MnS. This could be explained by leaking of small amounts of air into the reactor, which would prevent Mn$_3$O$_4$ from reducing. However, the proposed mechanism is still valid; in the oxidizing reactor, the material will always be quickly oxidized to Mn$_3$O$_4$, as shown in Figures (3.4) and (3.5). In the fuel reactor, the material thus always needs to go through reactions (3.1) and (3.2) in the presence of H$_2$S, leading to the observed formation of SO$_2$. In the complete absence of O$_2$ in the fuel reactor, reduction of Mn$_3$O$_4$ with H$_2$ to MnO and H$_2$O could be possible, which would occur in competition to reaction (3.1). Therefore, the undesired SO$_2$ formation is unavoidable under the given conditions. As a possible way for avoiding SO$_2$ formation in the fuel reactor, higher temperatures would also favor reduction of Mn$_3$O$_4$ to MnO by H$_2$, which is shown in the phase diagram in Figure (3.6).

**Figure 3.6:** Calculated phase diagram for the Mn-H-O system as a function of temperature. p(H$_2$) is fixed at $10^{-5}$ bar.

From this phase diagram, it is clear that MnO is preferred over Mn$_3$O$_4$ as the thermodynamically stable phase at higher temperatures and at lower partial pressures of O$_2$. If Mn$_3$O$_4$ is readily reduced to MnO in the presence of H$_2$, the formation of SO$_2$ (reaction (3.1)) might be minimized. However, operation of a gas cleaning reactor at temperatures above $\sim 850$ °C, which is typically the gasification temperature of biomass, contradicts the original idea of utilizing the temperature window in the gasification reactor or between gasification and subsequent catalytic conversion. In addition, even in full scale reactors operating at atmospheric pressures, it might be difficult to achieve an O$_2$ partial pressure below $10^{-10}$ bar, which is shown by the thermodynamic calculations in Figure (3.6) as the threshold between MnO and Mn$_3$O$_4$ at 850 °C. Therefore,
even under optimized conditions, the general validity of the proposed general CLD mechanism using Mn-based oxides holds true.

From the proposed mechanism, it becomes immediately clear that complete sulfur removal cannot be achieved with the tested materials under the given conditions, since there is always some generation of \( \text{SO}_2 \), which is undesired. Still, when integrated as reactive bed material in a dual fluidized bed gasifier, Mn based sorbents might remove a significant fraction of the sulfur from the fuel gas and thereby decrease the amount of organic sulfur leaving the gasification reactor, which would facilitate downstream gas cleaning.

With the combination of mass spectrometry data and X-ray absorption spectra, we are able to clearly identify Mn as the cause for the undesired \( \text{SO}_2 \) formation in the fuel reactor. Three methods to further improve sulfur removal seem possible: First, controlled oxidation of the Mn to avoid formation of \( \text{Mn}_3\text{O}_4 \), and instead to only form MnO. Since the oxidation of Mn proceeds very fast, this seems difficult to achieve and would require good control over the oxygen concentration and the residence time of the Mn sorbent in the oxidation reactor. Second, the material could be modified (e.g. by doping with other elements) so that formation of \( \text{Mn}_3\text{O}_4 \) is delayed or suppressed. For instance, ex situ XRD measurements showed that Mn supported on \( \gamma - \text{Al}_2\text{O}_3 \) formed MnAl2O4 upon oxidation, which was transformed back to MnS under sulfidation conditions. [106] Third, the concept could be modified, so that \( \text{Mn}_3\text{O}_4 \) is reduced to MnO in a sulfur-free, reducing atmosphere (e.g. the cleaned producer gas downstream), and subsequently be exposed to the sulfur-laden atmosphere. According to the thermodynamic considerations in Figure (3.6), this would require high temperatures and/or very low residual \( \text{O}_2 \) concentration.
3.6 Conclusion

In this chapter, simultaneous mass spectrometry and in situ X-ray absorption spectroscopy were employed to deduce the mechanism for sulfur transport over Mn-based materials which can be used for cleaning of biomass gasification derived producer gas. By exposing the material to transient gas atmosphere of reducing and oxidizing gas, the movement of the particles in a chemical looping reactor or in a dual fluidized bed gasifier was simulated. Analysis of the material’s performance for sulfur removal (derived from mass spectrometry) and its structure (derived from XAS) allowed proposing a 2-step mechanism in which Mn$_3$O$_4$ is transformed to MnS via MnO in the presence of H$_2$S, which removes most of the sulfur from the gas phase. Some unwanted SO$_2$ is generated under reducing conditions in the fuel reactor. Under oxidizing conditions, MnS is transformed back to Mn$_3$O$_4$ via MnO, producing SO$_2$ that can be separated from the producer gas. Two different samples, Mn on Mg-stabilized ZrO$_2$, and Mn impregnated on an attrition resistant, diatomite based support, showed similar results, which further corroborates the validity of this general mechanism.

Studying of the structure-performance relationship of Mn-based gas cleaning materials with XAS under reaction conditions in a time resolved fashion allows direct measurement of the changes in the sample structure. From this, mechanisms can be derived, which in turn allow knowledge based material and process development.
Chapter 4

High temperature desulfurization over molybdenum based catalysts

4.1 Abstract

Removal of sulfur species from biomass-gasification derived producer gas is required to protect downstream catalysts. Finding suitable materials for high temperature desulfurization is one main challenge for improvement of efficiency of catalytic biomass conversion. Biomass derived producer gas typically contains not only H$_2$S, but also organic sulfur species such as C$_4$H$_4$S, which are not removed by most sorbent materials. Here, we used Al$_2$O$_3$ supported Mo catalysts as bifunctional material for high temperature removal of H$_2$S and catalytic conversion of C$_4$H$_4$S.

By using X-ray absorption spectroscopy under reaction conditions, it is shown that H$_2$S is removed by sulfidation of MoO$_3$. C$_4$H$_4$S is catalytically converted over MoO$_2$ to MoS$_2$ and hydrocarbon species. Subsequent oxidation of MoS$_2$ to MoO$_3$ and SO$_2$ allows sequestration of sulfur from the gas stream. Furthermore, the negative effect of steam on sulfur removal is shown to be caused by competitive adsorption with sulfur species. These findings are expected to enable high-temperature desulfurization of biomass- or coal-derived gas for catalytic conversion, for instance to synthetic natural gas (SNG).

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The transmission electron micrographs of the sample in this chapter were supplied by Frank Krumeich at ETH Zürich, the sample preparation and most offline measurements were performed by Patrick Schuh from the Technische Universität München. Sylvia Köchli at PSI performed the inductively coupled plasma - optical emission spectroscopy (ICP-OES) measurements of the sample.
4.2 Introduction

Gasification of biomass feedstocks generates a gas mixture containing mainly of CO, H₂, CO₂, CH₄ and H₂O. In addition, depending on gasification parameters, several undesired byproducts and contaminants with different concentrations are produced. These include olefins, tars, sulfur and nitrogen heteroatom species (thiophene, pyridine), inorganic constituents including sulfur, chlorine and nitrogen (H₂S, COS, HCl, NH₃, HCN) and alkali metals. Sulfur containing compounds are corrosive to pipelines and downstream installations and thus limit plant lifetime. Moreover, sulfur species poison downstream catalysts, leading to significant negative impacts on catalyst performance: For example, already small amounts of H₂S poison the nickel or ruthenium catalysts used for methanation, hot gas cleaning, or Fischer-Tropsch synthesis.

In coal or biomass gasification process chains, sulfur components are often removed via low temperature processes (e.g. scrubbing), which includes cooling the producer gas from 850 °C (gasification temperature) below the dew point of water. Reheating up to 250 °C to 400 °C for downstream fuel catalysis as well as necessary re-evaporation of water for adjustment of the H₂ to CO ratio via steam reforming, and regeneration of scrubbing liquids, makes cold gas cleaning thermally inefficient and expensive. Technoeconomic analysis showed that processes like tar reforming, acid gas and sulfur removal comprise up to 31% of the minimal selling price for ethanol produced from biomass. This suggests that efficient sulfur and tar removal can lower costs significantly.

Hot gas desulfurization, operating between 300 °C and 850 °C would be preferable to improve the efficiency of biomass-to-fuel-conversion. Desulfurization over sorbent materials and / or catalysts will lead to accumulation of the sulfur on the sorbent material during time-on-stream. To maintain continuous operation, the sorbent needs to be replaced or regenerated; the latter either periodically (e.g. in a swing reactor design), or continuously. For continuous removal of sulfur from the gas stream, a chemical looping process can be used. For regeneration, the sorbent can be exposed to an oxidizing atmosphere which leads to production of SO₂, which is then sequestrated from the cleaned fuel gas stream.

One major challenge for hot gas desulfurization is identification of materials which remove different sulfur species from the gas in the presence of steam, while being stable over many cycles of sulfur uptake and regeneration. Zinc-titanate sorbents were proposed as regenerable, attrition resistant H₂S sorbents. The literature focuses however largely on the removal of H₂S from coal gas, ignoring organic sulfur compounds. Such organic sulfur compounds are also present in biomass-derived producer gas due to the low gasification temperature (compared to coal gasification), and are not removed by the high-temperature sorbents proposed in literature.

Molybdenum, together with Ni, Co or other promoters, removes sulfur containing components
4.2. INTRODUCTION

in the hydrodesulfurization (HDS) process in petroleum refining. [124] In contrast to the HDS process however, water vapor is always present in producer gas from the gasified biomass, either from the moist feedstock, or due to the use of steam as gasification medium. [3] Competitive adsorption of H$_2$O on the catalyst has been reported to reduce desulfurization of thiophene over Co-Mo catalysts, [125] in hydrodeoxygenation (HDO) over Ni-Mo [126] and Co-Mo catalysts [127] and in H$_2$S removal over ZnO. [128] Furthermore, the partial pressure of H$_2$ in the producer gas from atmospheric gasifiers is on the order several 100 mbar, while HDS reactors are typically operated at > 10 bar H$_2$ partial pressure. [124] As the biomass-derived synthesis gas has low partial pressures of H$_2$ and high amounts of steam, development of specific materials for the conditions in high-temperature desulfurization of biomass-derived synthesis gas is required.

Sulfidation of Mo catalysts and their HDS activity was intensively studied in the past with various techniques and the findings are summarized in reviews. [129, 130] Mo-based catalysts for HDS are usually regarded as slabs of MoS$_2$, terminated by S, and eventually doped with Co on the edges of the slab. [131] The active sites are assumed to be vacancies on the edges of MoS$_2$. Furthermore, in HDS, thiophene is continuously converted to H$_2$S which is eliminated downstream in a ZnO bed, [124] whereas in hot gas desulfurization processes, ideally all sulfur is converted to SO$_2$ and sequestrated from the synthesis gas stream. For these reasons, sulfide catalysts, as they are typically employed in HDS under high H$_2$ partial pressures, cannot be used for hot gas desulfurization of biomass with continuous regeneration, since the sulfur on the catalyst would be immediately oxidized to SO$_2$ upon regeneration.

In this chapter, mechanisms of sulfur removal are investigated in a cyclic process from gasified biomass at high temperature. The goal is to develop high temperature gas cleaning and to understand the mechanisms for removal of H$_2$S and organic sulfur species, which are rarely considered in high-temperature gas cleaning studies. As Mo-based catalysts are often used for conversion of organic sulfur species, Mo is a promising material to accomplish sulfur removal. However, cyclic operation of sulfur removal and regeneration leads to requirements for the material, that are different from those under HDS conditions, which is typically performed at lower temperatures, at much higher H$_2$ partial pressures and with significantly lower steam content. For studying the state of the Mo under reaction conditions, in situ X-ray absorption spectroscopy was employed. Recent advances in synchrotron instrumentation allow in situ studies on a time scales of seconds or sub-second, which are relevant for dynamic processes, such as chemical looping processes. [132] The mechanism for removal of H$_2$S was found to be concurrent sulfidation of MoO$_3$ to MoS$_2$ and reduction to MoO$_2$. Removal of C$_4$H$_4$S proceeds via desulfurization of the C$_4$H$_4$S ring, leading to sulfidation of MoO$_2$. 
4.3 Experimental approach

4.3.1 Materials

The materials were prepared by repeated wetness impregnation. Ammonium heptamolybdate tetrahydrate \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \times 4\text{H}_2\text{O, SigmaAldrich})\) was dissolved in deionized water and impregnated on \(\gamma - \text{Al}_2\text{O}_3\) support (Sasol). Excess water was slowly evaporated under vacuum, and the impregnated support was washed with deionized water. Finally, the catalyst was dried at 110 °C for 1 h and calcined at 600 °C for 6 h. This procedure was repeated four times to increase the Mo loading. Approximately 25 mg of the sample were used for the in situ experiments with \(\text{H}_2\text{S}\) and \(\text{C}_4\text{H}_4\text{S}\). The reference compounds of \(\text{MoO}_2\), \(\text{MoO}_3\), \(\text{MoS}_2\) were purchased from SigmaAldrich, mixed with cellulose and pressed into pellets. Samples were characterized by \(\text{N}_2\) physisorption, X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES) and scanning transmission electron microscopy (STEM). STEM was performed on a Hitachi HD2700CS microscope.

4.3.2 Experimental setup

The reactor for the in situ experiments consisted of a quartz capillary (3 mm outer diameter, 0.1 mm wall thickness, Hilgenberg) that was heated by a hot air blower (Leister). The samples were fitted in the reactor between two plugs of quartz wool. The temperature inside the capillary was measured with a thermocouple, placed downstream of the bed, and was kept at 600 °C. The pressure inside the reactor was kept constant at 0.5 bar overpressure by pressure regulating valves (Bronkhorst). A computer controlled setup was used to mix gases using mass flow controllers (Bronkhorst). All gas lines were coated with amorphous SiO\(_2\) to minimize sulfur adsorption (Sulfinert, Restek). Gas analysis was performed using a quadrupole mass spectrometer (Max 300-LG, Extrel). Deionized water was injected into the gas stream by a syringe pump (Harvard apparatus) through a fused silica capillary into a crosspiece in a heated box. Since this method has limited dynamics of starting and stopping the water feed, steam flow was constant during the experiments with steam. The transfer lines between the crosspiece, the reactor and the mass spectrometer were heated to avoid condensation.

4.3.3 XAS setup

The in situ XAS experiments at the Mo K-edge (20.0 keV) were performed in transmission mode at the SuperXAS beamline at the Swiss Light Source, using a QuickXAS monochromator with a channel-cut Si-111 crystal that was rotated at a frequency of 0.2 Hz, resulting in 5 s time resolution per spectrum. The X-ray energy was calibrated using a Mo metal foil, placed downstream of the sample. The beam intensity was monitored with ion chambers, filled with \(\text{N}_2\) (%0,}
4.3. EXPERIMENTAL APPROACH

before the sample), and Ar (I₁ and I₂, after the sample and the reference foil, respectively). The X-ray beam was focused to approximately 100 µm² with a Pt-coated toroidal mirror. Normalization, energy calibration, linear combination fitting and EXAFS fitting was performed with IFEFFIT. EXAFS fitting of the fresh catalyst sample was performed over a k-range from 3 to 14 Å⁻¹ in k² weighting. The value for S₀² (0.87) was derived from fitting a spectrum of Mo foil, acquired under identical experimental conditions. Linear combination fitting was performed over a range of -20 to + 50 eV, relative to the absorption edge. All single components used the same energy shift E₀ and were forced to have a weight between 0 and 1. Summing of the components to 1 was not enforced.
4.4 Results

4.4.1 Characterization of the fresh catalyst

To characterize the local structure of the fresh, calcined catalyst, the sample was investigated with X-ray absorption spectroscopy. X-ray absorption near edge structure (XANES) spectra of the fresh Mo/Al\(_2\)O\(_3\) catalyst, along with spectra of reference compounds are shown in Figure (4.1a). The XANES spectra of the fresh catalyst exhibit features that are very similar to those of reference MoO\(_3\) sample, such as the shoulder in the spectrum at 20005 eV and the position of the absorption edge. This qualitative comparison suggests that the fresh Mo catalyst is oxidized to MoO\(_3\) after calcination. The corresponding Fourier transforms of the full extended X-ray absorption fine structure (EXAFS) spectra are shown in Figure (4.1b). In the Fourier transforms, the fresh catalyst shows one peak at \(\sim 1.2\ \text{Å}\), but no significant peaks at higher distances. Compared to the Fourier transforms of the references, it can be concluded that this peak is a Mo-O scattering shell at a similar bond distance as in the MoO\(_3\) reference spectra. According to the XANES and EXAFS spectra, the fresh catalyst is identified as MoO\(_3\). However, unlike the reference spectra, the fresh MoO\(_3\)/Al\(_2\)O\(_3\) sample shows only weak scattering shells at higher distances (such as the Mo-Mo scattering shell at \(\sim 1.8\ \text{Å}\)), which suggests a small particle size.

![Figure 4.1](image.png)

**Figure 4.1:** Fresh calcined catalyst sample Mo/Al\(_2\)O\(_3\) compared with Mo reference compounds for MoO\(_3\), MoO\(_2\), MoS\(_2\) and Mo foil. a) Mo K-edge XANES spectra. b) Fourier transforms of the EXAFS spectra.

Fitting the EXAFS spectrum of the fresh catalyst with a MoO\(_3\) reference structure \([133]\) yields a coordination number of 3.7 ± 0.5 for the Mo-O shell at a distance of 1.71 ± 0.01 Å with a
4.4. RESULTS

Debye Waller factor of 0.005 ± 0.001 Å². No scattering shells at higher distances could be fitted. Scanning transmission electron microscopy of the fresh MoO₃/Al₂O₃ catalyst (see Figure (4.2)) reveals a particle size of ~ 1 nm, supporting the findings of the EXAFS analysis.

![STEM micrograph of the fresh Mo/Al₂O₃ catalyst as measured in Z-contrast mode. The bright dots are the Mo clusters.](image)

To investigate the effect of Mo impregnation on the surface area and pore volume of the catalyst particles, N₂ physisorption measurements were performed. The blank Al₂O₃ support showed a surface area of 170 m² g⁻¹ (measured with the Brunauer, Emmett, Teller (BET) method [134]) and a pore volume (according to the Barrett-Joyner-Halenda method [135]) of 0.46 cm³ g⁻¹, while for the fresh MoO₃ / Al₂O₃ (4 × impregnated) a BET surface area of 180 m² g⁻¹ and a pore volume of 0.45 cm³ g⁻¹ were measured. According to these results, impregnation and calcination of the support changes the porous structure only slightly. The impregnation resulted in 9 wt-% loading of Mo on the Al₂O₃ support, as measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

4.4.2 Removal of H₂S under dry conditions

In producer gas from biomass or coal gasification, H₂S is usually the most abundant sulfur species. We therefore first investigated removal of H₂S under dry conditions. The fresh catalyst was heated to 600 °C and exposed to periodically changing atmosphere, simulating the conditions in a chemical looping desulfurization reactor. After reduction in 1.25 % H₂ for 180 seconds, 2000 ppm H₂S were added to the total feed of 25 ml min⁻¹ for 900 seconds, corresponding to a total sulfur amount of 33.5 µ-mol. This represents the reducing conditions of sulfur-containing producer gas, which typically also contains CO, CO₂ and CH₄. Following a purge in He for 60 seconds, the catalyst was oxidized in 4 % O₂ for 180 seconds to regenerate the sample. The cycles were repeated 10 times. In Figure (4.3), selected mass spectrometer traces for H₂ (m/z...
2), H₂S and O₂ (both measured on m/z 33) and SO₂ (m/z 64) of one representative cycle of reduction, sulfidation and regeneration at 600 °C are shown.

![Figure 4.3](image)

**Figure 4.3:** Cyclic exposure of Mo/Al₂O₃ catalyst at 600 °C to reduction in H₂, sulfidation in H₂ + H₂S, and oxidation in O₂. Selected mass spectrometer traces of one cycle (top panel) for reactor outlet are shown together with sample composition, derived from linear combination fitting of Mo K-edge XANES spectra.

While H₂S is not detected at the reactor outlet during exposure to 2000 ppm H₂S within 900 s, SO₂ is detected upon oxidation with 4 % O₂. One measure for stability of this process is the amount of SO₂ that is generated during each cycle upon oxidation, which is shown in Figure (4.4) as the integrated signal of m/z 64 over 10 cycles. These data suggest that H₂S is effectively removed by the Mo/Al₂O₃ catalyst from the producer gas stream over multiple cycles, and oxidized to SO₂. The resulting SO₂ stream can be separated when the oxidation is performed in a separate reactor, for instance in a chemical looping reactor or a swing reactor concept.

To gain insight into the mechanism of sulfur removal by the Mo-based catalyst, time resolved in situ X-ray absorption spectroscopy at the Mo K-edge was employed during the cycles of reduction, sulfidation and oxidation. The XAS spectra were averaged over 10 cycles. Linear combination fitting (LCF) can be used to fit the percentage of known reference states of the catalyst. Applying LCF to time resolved XAS spectra allows detection of trends in the reaction. The spectra were fitted with three components, MoO₃, MoO₂ and MoS₂. Here, the spectrum of the fresh catalyst (see Figure (4.1)) was used as reference for MoO₃, as the MoO₃ nanoparticles differ slightly in their XANES signal from the MoO₃ reference sample. LCF fits of selected XANES spectra at the beginning of sulfidation in H₂S, during sulfidation, at the end of sulfidation, and after oxidation, are shown in Figure (4.5).
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The resulting composition over one cycle of sulfidation and oxidation is shown in Figure (4.3). The LCF results indicate that the Mo catalyst is fully oxidized to MoO$_3$ upon exposure to 4 % O$_2$ within a few seconds. The difference between 1 and the sum of the three fractions, i.e. the unfitted fraction, is shown as black line. The unfitted fraction never exceeded 2 %, indicating a good fit of the XANES data with the three selected references. Exposure to 1.25 % H$_2$ does not substantially reduce the catalyst, and even a small fraction of MoS$_2$ is detected by LCF. However, upon exposure to 2000 ppm H$_2$S, MoO$_3$ is consumed while MoO$_2$ and MoS$_2$ are formed at a similar rate. At the end of the sulfidation period, approximately 50 % of the sample in the X-ray beam is MoO$_3$, 30 % is sulfided to MoS$_2$, and 20 % is in the form MoO$_2$.

While the XANES region (up to 100 eV above the absorption edge) probes the electronic structure of the sample, the local geometric environment around the absorbing element is probed by the EXAFS part of the spectrum. The Fourier transforms of selected EXAFS spectra during the sulfidation and regeneration cycle are shown in Figure (4.5)b. After oxidation, a single peak at $\sim 1.2$ Å (not phase corrected) is visible at a similar position as in the fresh, calcined sample (see Figure (4.1)), indicating full oxidation to MoO$_3$. Upon exposure to H$_2$, this peak’s intensity decreases, while a second peak at $\sim 1.7$ Å appears. Over the course of sulfidation, the peak at 1.2 Å further decreases in intensity, while the peak at 1.7 Å increases in intensity and shifts to higher distances. The peak at 1.2 Å can be attributed to the Mo-O scattering shell of MoO$_3$, while Mo-O and Mo-S scattering shells of MoO$_2$ and MoS$_2$ respectively, have peaks between 1.5 and 2 Å. This suggests that the fraction of MoO$_3$ in the sample decreases over time, while the fractions of MoO$_2$ and of MoS$_2$ grow. Fitting of the full EXAFS spectra of such mixtures, with many scattering paths overlapping at similar bond lengths, is not possible with the data quality obtained here. Nevertheless, the qualitative interpretation of the EXAFS spectra supports the findings of LCF of the XANES spectra in Figure (4.3).

Figure 4.4: Integrated SO$_2$ signal (m/z 64) over 10 cycles of H$_2$S exposure to Mo/Al$_2$O$_3$ at 600 °C.
4.4.3 Removal of H$_2$S in the presence of steam

All woody biomass contains moisture, with contents varying between 6.5 % (for fir) and 60 % (for willow). In addition, steam is often used as gasification medium. Consequently, the producer gas after biomass gasification contains rather large amounts of steam. Therefore, it is imperative that any high-temperature gas cleaning operates reliably in the presence of steam, since condensation to remove steam would require cooling, which is to be avoided. The experiment of reduction, H$_2$S removal and oxidation was repeated with additional steam, and the mass of the catalyst in the reactor was varied. The water feed rate was 0.1 ml h$^{-1}$ of liquid water, corresponding to $\sim$ 7.7 % steam content at a dry gas flow rate of 25 ml min$^{-1}$. In Figure 4.6, the integrated H$_2$S signals at the reactor outlet are shown, normalized to the He signal and averaged over 10 - 15 cycles. For comparison, the integrated signal of the dry experiment is given.

While the presence of steam reduces the H$_2$S uptake of 25 mg catalyst by $\sim$ 40 % compared to dry conditions, higher amounts of catalyst lead to almost complete H$_2$S removal even in the presence of steam. This indicates that the presence of steam reduces H$_2$S removal, but can be compensated for by using a larger amount of catalyst. Such effect can be rationalized by
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Figure 4.6: Integrated \( \text{H}_2\text{S} \) signal at the reactor outlet (measured by m/z 33) for different catalyst masses under identical experimental conditions at 600 °C with 7.7 % steam. The data for mass of 0 g represents the measurement through an empty tube. For comparison, the data from the dry experiment for mass 25 mg is shown as empty triangle.

competitive adsorption, where \( \text{H}_2\text{O} \) occupies surface sites of the Mo catalyst, slowing down the reaction of \( \text{H}_2\text{S} \).

4.4.4 Removal of \( \text{C}_4\text{H}_4\text{S} \) under dry conditions

In producer gas from gasified biomass, sulfur is not only present as \( \text{H}_2\text{S} \), but also as organic sulfur compounds, which also need to be removed from the gas stream. As a model compound for organic sulfur species, thiophene (\( \text{C}_4\text{H}_4\text{S} \)) was chosen in this study. Similar to the cyclic sulfidation under \( \text{H}_2\text{S} \) (see above), the catalyst was exposed to periodic reduction, exposure to \( \text{H}_2 + \text{C}_4\text{H}_4\text{S} \) and oxidation at a constant temperature of 600 °C. Comparison of the mass spectrometer data for the reactor inlet (dashed lines) and the reactor outlet (solid lines) in Figure (4.7) shows that all 200 ppm \( \text{C}_4\text{H}_4\text{S} \) (m/z 84) that the Mo catalyst is exposed to, is removed in the presence of 40 % \( \text{H}_2 \). Upon oxidation, \( \text{SO}_2 \) is generated, indicating that sulfur was bound to the Mo/\( \text{Al}_2\text{O}_3 \), and oxidized in 4 % \( \text{O}_2 \). A control experiment with blank \( \text{Al}_2\text{O}_3 \) support under identical conditions showed no detectable interaction of \( \text{Al}_2\text{O}_3 \) with \( \text{C}_4\text{H}_4\text{S} \) (data not shown). The removal of \( \text{C}_4\text{H}_4\text{S} \) from the gas stream can therefore be attributed to the Mo particles.

Linear combination fitting was performed on the time resolved XANES data of one averaged cycle of reduction, exposure to \( \text{H}_2 + \text{C}_4\text{H}_4\text{S} \) and subsequent oxidation. The LCF results in Figure (4.7) show that the MoO\(_3\) is readily reduced to \( \sim 30 \% \text{ MoO}_2 \) and 70 % \( \text{MoO}_3 \) after exposure to 40 % \( \text{H}_2 \). Compared to the experiment with \( \text{H}_2\text{S} \) uptake (Figure (4.3)), the amount
of produced MoO$_2$ is higher, due to the higher H$_2$ concentration. Over the time on stream during exposure to 40 % H$_2$ + 200 ppm C$_4$H$_4$S, the Mo catalyst is slowly reduced further. Upon oxidation in 4 % O$_2$, Mo is completely oxidized to MoO$_3$.

In contrast to the experiment with H$_2$S, no significant fraction of MoS$_2$ is found. Within 15 minutes, the catalyst is exposed to approximately 3.3 $\mu$-mol C$_4$H$_4$S. In the experiment with sulfidation by H$_2$S (see above), approximately 30 % of the Mo catalyst in the X-ray beam is sulfided to MoS$_2$ after exposure to 33.5 $\mu$-mol H$_2$S. Therefore, exposure to 3.3 $\mu$-mol C$_4$H$_4$S is expected to result in approximately 3 % of the Mo being in the MoS$_2$ phase, which is below the detection limit of LCF of XAS spectra (typically 5 - 10 %).

The Fourier transformed EXAFS spectra, shown in Figure 4.8, present a similar qualitative picture as the LCF results. Upon reduction, the intensity of the scattering shell at $\sim 1.2$ Å decreases, while a scattering shell at $\sim 1.8$ Å appears. The first peak at 1.2 Å can be attributed to the first Mo-O coordination shell from MoO$_3$, and the scattering shell at 1.8 Å can be assigned to the first Mo-O coordination shell from MoO$_2$ (see reference spectra in Figure 4.1).

Modulated excitation spectroscopy was shown to enhance the fitting precision of XAS spectra by filtering out all those parts in the spectrum that do not follow the excitation frequency, which

Figure 4.7: Cyclic exposure of Mo/Al$_2$O$_3$ catalyst at 600 °C to reduction in H$_2$, reduction in H$_2$ + C$_4$H$_4$S, and oxidation in O$_2$. Selected mass spectrometer traces for reactor inlet (dashed line) and outlet (solid lines) are shown together with sample composition (bottom panel), derived from linear combination fitting of Mo K-edge XANES.
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Figure 4.8: Selected Fourier transforms of XAS spectra during cyclic exposure of Mo/Al₂O₃ catalyst to H₂, H₂ + C₄H₄S and O₂ at 600 °C.

is here the switching of the gas feed (see also chapter [2]). The remaining spectra, called demodulated or phase-detected spectra, are essentially difference spectra between the different states of the catalyst during one excitation cycle, but with better signal-to-noise ratio and containing only those contributions to the spectra that change upon the excitation. While the XANES or the EXAFS data in Figures (4.7) and (4.8) provide no conclusive evidence for formation of MoS₂, the demodulation of the spectra, which are modulated with the switching of gases allows sensitive detection of minute changes in the sample’s structure. [67] The demodulation of the spectra transforms them from the time domain into a phase domain. Selected demodulated spectra are shown in Figure (4.9) in k-space and R-space for different phase angles Φ_k.

The demodulated spectra in k-space show that there are at least two different contributions to the spectra, with the major contribution at Φ_k = 310°, and the minor contribution at Φ_k = 223°. The two spectra show a distinctly different shape with strong contributions at different values of k. Fourier transformation of the demodulated spectra at Φ_k = 310° and Φ_k = 223° to R-space shows those scattering shells that change upon the excitation, i.e. the switching of gas atmosphere from H₂ to H₂ + C₄H₄S and to O₂. For qualitative comparison, they are plotted together with difference spectra of reference compounds of MoO₃, MoO₂ and MoS₂. This comparison indicates that the demodulated spectrum at 310° is similar to the difference spectrum of MoO₃ and MoO₂ between 1 and 2 Å, indicating that this spectrum corresponds to reduction of MoO₃ to MoO₂ of a fraction of the sample. The peak of the demodulated spectrum at 223° at R ~ 1.7 Å is in phase with the difference spectrum of MoO₂ and MoS₂, which is
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Figure 4.9: Selected demodulated XAS spectra during cyclic exposure of Mo/Al₂O₃ catalyst to H₂, H₂ + C₄H₄S and O₂ at 600 °C. The spectrum at 223° is displayed as red thick line b) Fourier transforms of selected demodulated XAS spectra and of difference spectra of reference compounds.

indicative of the sulfidation of MoO₂ to MoS₂. The amplitude of the demodulated spectrum at 223° is ~ 10 times smaller compared to the spectrum at 310°, which indicates that a much smaller fraction of Mo atoms is sulfided. In conclusion, the demodulated spectra suggest that the sample undergoes transition from MoO₃ to MoO₂, which is already confirmed by LCF of XANES spectra. Furthermore, a fraction of the sample is transformed from MoO₂ to MoS₂, which is not readily visible in the XANES or EXAFS spectra.

Influence of pre-reduction on C₄H₄S removal

In a cyclic process, where the catalyst is exposed to alternating atmosphere of sulfur containing producer gas, which is usually reducing, and oxidizing gas for regeneration, the oxidation state of the majority of Mo atoms is changing (see Figure (4.3)). To study the effect of the oxidation state of Mo on C₄H₄S removal, the duration of reduction before addition of C₄H₄S was varied. In Figure (4.10), the C₄H₄S signal at the reactor outlet is shown for different durations of reduction. It was found that the removal of C₄H₄S from the gas stream depends on the time of previous reduction. The amount of C₄H₄S that is detected at the reactor outlet drops over time-on-stream, which coincides with progressing reduction of MoO₃ to MoO₂ (see Figure (4.7)). For longer times of pre-reduction, the amount of C₄H₄S that is detected upon addition of C₄H₄S to the stream is lowered. This suggests that MoO₂ is more favorable for C₄H₄S removal than MoO₃.
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Figure 4.10: \( C_4H_4S \) signal (measured by m/z 84) over time during cyclic reduction, exposure to \( H_2 + C_4H_4S \) and oxidation for different times of pre-reduction.

Influence of \( H_2 \) on \( C_4H_4S \) removal

While the removal of \( C_4H_4S \) under dry conditions is accomplished in the cyclic process, as shown above, the above results do not clarify if the removal of \( C_4H_4S \) is due to pure sorption of \( C_4H_4S \) to MoO\(_2\), or if it is a catalytic process. To study this, the cycles of reduction, exposure to \( C_4H_4S \) and oxidation were modified, such that simultaneous feed of \( H_2 \) and \( C_4H_4S \) was compared to a feed of \( C_4H_4S \) without \( H_2 \). In both cases, the catalyst was reduced in 40 % \( H_2 \) before addition of 200 ppm \( C_4H_4S \), since it was shown above that a previously reduced catalyst is required for \( C_4H_4S \) conversion. If the presence of \( H_2 \) has an impact on the removal of \( C_4H_4S \), it participates in a catalytic process. Otherwise, the removal of \( C_4H_4S \) can be described as pure sorption.

In Figure 4.11, the integrated \( C_4H_4S \) signal (measured as m/z 84) is shown for the reactor inlet, the reactor outlet with only \( C_4H_4S \) in the feed, and simultaneous feed of \( H_2 \) and \( C_4H_4S \). As before, all experiments were performed at 600 °C. In the absence of \( H_2 \), approximately 40 % of the \( C_4H_4S \) that is sent into the reactor is measured at the outlet, so that 60 % are sorbed to the sample. When \( H_2 \) is fed simultaneously, no \( C_4H_4S \) is detected at the outlet. This suggests that the removal of \( C_4H_4S \) over a pre-reduced Mo catalyst proceeds at least partially catalytically, most likely due to hydrogenation of \( C_4H_4S \) to \( H_2S \) and \( C_4H_6 \) and other hydrocarbons. The experiment in the absence of \( H_2 \) shows that a fraction of the \( C_4H_4S \) is however removed from the gas stream by sorption to the catalyst.
Figure 4.11: Integrated $C_4H_4S$ signal (measured by m/z 84) at the reactor inlet (cycles 1 and 2), and at the reactor outlet in the absence of $H_2$ (cycles 3 - 7) and in the presence of $H_2$ (cycles 8 - 10).

Influence of sulfidation on $C_4H_4S$ removal

The decomposition of $C_4H_4S$ in the presence of $H_2$ (see previous paragraph) will most likely lead to sulfidation of the Mo catalyst (see Figure 4.9). Since the sulfidation of Mo by $H_2S$ (either from the feed, or from hydrogenation of $C_4H_4S$) and $C_4H_4S$ removal occur in parallel, it is important to understand the influence of sulfidation of the catalyst on $C_4H_4S$ removal. To test this, 50 mg of the Mo/Al$_2$O$_3$ catalyst was pre-sulfided before exposure to $C_4H_4S$. After approximately 220 minutes sulfidation at 600 °C in 40 % $H_2$ + 1000 ppm $H_2S$, the catalyst was exposed to 40 % $H_2$ + 100 ppm $C_4H_4S$ at 600 °C. Selected MS traces during sulfidation and subsequent $C_4H_4S$ exposure are shown in Figure 4.12. After sulfidation, all $C_4H_4S$ was removed, while small amounts of $H_2S$ and butadiene ($C_4H_6$) were generated. This confirms that a sulfided Mo catalyst is also active for removal of $C_4H_4S$ from the gas stream as was expected based on its use in HDS applications.

Breakthrough of $C_4H_4S$

For a better understanding of the mechanisms of $C_4H_4S$ removal, a breakthrough experiment was performed under steady-state conditions, of which selected mass spectrometer traces are shown in Figure 4.13.

Following reduction in 40 % $H_2$ for 6 minutes, 25 mg of the catalyst was exposed to 40 % $H_2$ and 100 ppm $C_4H_4S$ at 600 °C at a total gas flow rate of 25 ml min$^{-1}$. At the beginning of the exposure, no $H_2S$ (m/z 33) or $C_4H_4S$ (m/z 84) is measured at the reactor outlet, as in the previous dry experiments. Approximately 2700 seconds (45 minutes) after the start of $C_4H_4S$
Figure 4.12: Selected mass spectrometer traces during the sulfidation and subsequent exposure to $H_2 + C_4H_4S$ of the Mo/Al$_2$O$_3$ catalyst at 600 °C.

Figure 4.13: Selected mass spectrometer traces during continuous exposure of the Mo/Al$_2$O$_3$ catalyst to $H_2 + C_4H_4S$ at 600 °C.

exposure, $C_4H_4S$ is detected at the reactor outlet, together with $H_2S$. Throughout the next 5 h, the signals for $C_4H_4S$ and $H_2S$ slowly rise, and eventually reach a steady state. In addition, various C1-C4 species are detected. Before breakthrough of $C_4H_4S$, $CH_4$ (m/z 15), $C_2H_4$ (m/z 26 and 27) and $C_2H_6$ (m/z 27, 30) are detected, together with $C_4H_8$ (m/z 27, 28 and 41) and
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When C₄H₄S breaks through, the signals CH₄, C₂H₄, C₂H₆ and C₄H₁₀ reach a maximum. After breakthrough, signals for CH₄ and C₂H₆ decrease to almost zero, signals of C₂H₄ and C₄H₁₀ return to near initial levels, and C₄H₆ (m/z 54) is detected.

These data indicate that over the time-on-stream of continuous exposure to H₂ + C₄H₄S, the selectivity towards C conversion changes. In the beginning, some of the carbon rings of C₄H₄S are cracked to C₁ and C₂ species. After C₄H₄S breakthrough, the selectivity shifts towards C₃ and C₄ species. While the detailed mechanism for selectivity towards different carbon species is beyond the scope of this study, the results clearly indicate a shift in selectivity that coincides with C₄H₄S breakthrough.

4.4.5 Removal of C₄H₄S in the presence of steam

To assess the influence of steam on the removal of C₄H₄S, the cyclic experiments of reduction, exposure to C₄H₄S and oxidation (see Figure 4.7) were repeated in the presence of 7.7 % steam in the feed. Selected mass spectrometer traces of one representative cycle are shown in Figure 4.14.

![Figure 4.14: Cyclic exposure of the Mo/Al₂O₃ catalyst at 600 °C to reduction in H₂, reduction in H₂ + C₄H₄S, and oxidation in O₂, all in the presence of 7.7 % steam. Selected mass spectrometer traces (top panel) for reactor inlet (dashed line) and outlet (solid lines) are shown together with sample composition, derived from linear combination fitting of Mo K-edge XANES.](image)
In contrast to the dry experiment, the mass spectrometer results show only partial conversion of C$_4$H$_4$S. Directly after addition to the gas feed, the C$_4$H$_4$S signal, measured at the reactor outlet, is $\sim 60\%$ that of the inlet signal. The sample’s composition, determined by LCF of the time resolved XAS spectra, suggests no qualitative difference to the dry experiment (see Figure 4.7). Upon addition of H$_2$, $\sim 40\%$ of the sample is reduced from MoO$_3$ to MoO$_2$, which is quickly oxidized to MoO$_3$ upon oxidation in O$_2$. The degree or speed of reduction and oxidation are not changed significantly upon addition of steam.

Similar to the experiment on H$_2$S uptake (see above), the amount of catalyst in the reactor was varied while all other experimental parameters were kept constant during reduction, exposure to C$_4$H$_4$S and oxidation, in the presence of steam. In Figure 4.15, the integrated signal for C$_4$H$_4$S at the reactor outlet is shown. The mass spectrometer data for m/z 84 (C$_4$H$_4$S) was normalized to the He signal (m/z 4), integrated over single cycles, and the mean values and standard deviations were calculated for data from 13 - 15 cycles.

![Figure 4.15: Integrated C$_4$H$_4$S signal at the reactor outlet (measured by m/z 84) for different catalyst masses under identical experimental conditions at 600 °C with 7.7 % steam. The data for mass of 0 g represents the measurement through an empty tube. For comparison, the data from the dry experiment for mass 25 mg is shown as empty triangle.](image)

While the resulting standard deviations are relatively large, the trend shows that with increasing catalyst mass a lower C$_4$H$_4$S signal is detected at the outlet. This indicates that the detrimental effect of steam is due to competitive adsorption of H$_2$O on the MoO$_2$ surface, blocking sites for C$_4$H$_4$S to adsorb. This effect can be compensated for by using more catalyst material. For comparison, the data for 25 mg catalyst mass from the dry experiment is shown, where no C$_4$H$_4$S is measured at the reactor outlet.
4.5 Discussion

4.5.1 Mechanism of sulfur removal

The results for reactivity (measured by mass spectrometry) and structure of the Mo catalyst (measured by XAS) allows proposing mechanisms for sulfur removal. These proposed mechanisms of removal of $\text{H}_2\text{S}$ and $\text{C}_4\text{H}_4\text{S}$ over Mo are schematically displayed in Figure (4.16) and are discussed in the following.

![Figure 4.16: Schematic representation of the mechanisms during $\text{H}_2\text{S}$ removal and $\text{C}_4\text{H}_4\text{S}$ removal. The different colors represent the different phases ($\text{MoO}_3$, $\text{MoO}_2$, $\text{MoS}_2$), according to the color code in Figure (4.3, 4.7, 4.14).](image)

From the experiments on uptake of inorganic sulfur ($\text{H}_2\text{S}$) (see Figures (4.3, 4.6), it can be concluded that the removal of $\text{H}_2\text{S}$ from the producer gas occurs by sulfidation of $\text{MoO}_3$ to $\text{MoS}_2$ under concurrent formation of $\text{MoO}_2$. Under oxidizing atmosphere, $\text{MoS}_2$ is oxidized to $\text{MoO}_3$, while $\text{SO}_2$ is released.

\begin{align}
\text{Sulfidation} \\
2\text{MoO}_3 + 2\text{H}_2 + 2\text{H}_2\text{S} &\rightarrow \text{MoO}_2 + \text{MoS}_2 + 4\text{H}_2\text{O} \quad (4.1) \\
\text{Regeneration} \\
2\text{MoS}_2 + 7\text{O}_2 &\rightarrow 2\text{MoO}_3 + 4\text{SO}_2 \quad (4.2)
\end{align}

This mechanism is in line with earlier findings, which indicated that $\text{MoO}_3$ is sulfided to $\text{MoS}_2$. 
by O-S exchange, followed by reduction. Temperature programmed sulfidation experiments showed that MoO$_3$ supported on Al$_2$O$_3$ can be sulfided already at 500 K via O-S exchange on Mo$^{(VI)}$ ions, followed by reduction to Mo$^{(IV)}$. This was later supported by X-ray photoelectron spectroscopy (XPS) and infrared emission spectroscopy on crystalline MoO$_3$, by XPS on SiO$_2$ supported MoO$_3$ model catalysts and by XAS and transmission electron microscopy (TEM) studies on MoO$_3$/SiO$_2$ catalysts.

For the removal of organic sulfur (C$_4$H$_4$S), a MoO$_2$ surface is preferred over a MoO$_3$ surface (see Figure 4.11). From the experiments of C$_4$H$_4$S removal, several mechanisms for the removal are plausible:

1. C$_4$H$_4$S can adsorb to the MoO$_2$ surface, where it does not react further, until all possible sites are occupied (sorption).
2. C$_4$H$_4$S adsorbs to the MoO$_2$ surface, where it is hydrogenated by H$_2$ to H$_2$S and hydrocarbons, mostly C4 and only small amounts of C1 - C3 species (hydrogenolysis).
3. The adsorbed C$_4$H$_4$S can directly sulfide the Mo site to which it adsorbs, forming C1 - C4 hydrocarbons (direct desulfurization).

In the case of mechanism (1), the only measured species after all Mo sites are occupied would be C$_4$H$_4$S. Mechanism (2) would lead to detection of H$_2$S and hydrocarbons after breakthrough, while direct desulfurization (mechanism (3)) would result in breakthrough of C$_4$H$_4$S and hydrocarbons.

From the presented data, it can be concluded that the mechanism for C$_4$H$_4$S removal is not pure sorption (mechanism (1)) of the C$_4$H$_4$S molecule to the MoO$_2$ surface, since H$_2$ is required to remove all C$_4$H$_4$S from the gas (see Figure 4.11), indicating a catalytic process. Demodulation of the XAS spectra (see Figure 4.9) suggests that a fraction of the catalyst undergoes transition from MoO$_2$ to MoS$_2$ during exposure to H$_2$ and C$_4$H$_4$S.

The breakthrough of C$_4$H$_4$S with some production of H$_2$S indicates that hydrogenolysis is not the prevailing mechanism of C$_4$H$_4$S removal over MoO$_2$. If that was the case, as it is for presulfided Mo (see Figure 4.12), only H$_2$S would be observed in the breakthrough experiment, but no C$_4$H$_4$S.

For these reasons, we conclude that C$_4$H$_4$S is removed over MoO$_2$ mainly through direct desulfurization of C$_4$H$_4$S. Initially, sulfur-free surfaces are being covered with C$_4$H$_4$S, removing all C$_4$H$_4$S from the gas. In the presence of H$_2$, the adsorbed C$_4$H$_4$S then sulfides the MoO$_2$ while hydrocarbons are released. The observation of CH$_4$ in this initial phase indicates that the carbon structure is completely cracked to C1, perhaps due to the presence of acid sites on MoO$_2$. This process occurs at a slower rate than the feed of C$_4$H$_4$S, leading to the observed breakthrough of C$_4$H$_4$S.

**Direct desulfurization**

$$H_2 + C_4H_4S + MoO_2 \rightarrow MoS_2 + CH_4 + C2 - C4 - species$$  \hspace{1cm} (4.3)
Hydrodesulfurization

\[
H_2 + MoS_2 + C_4H_4S \rightarrow MoS_2 + H_2S + C_4 - \text{species}
\]  

(4.4)

The MoS\(_2\) phase that is formed by sulfidation in H\(_2\)S is active for removal of C\(_4\)H\(_4\)S in the presence of H\(_2\) (see Figure 4.11), forming butadiene (C\(_4\)H\(_6\)) and H\(_2\)S.

4.5.2 Influence of steam

Steam, which is always present in producer gas from gasified biomass, has a detrimental influence on the desulfurization over Mo/Al\(_2\)O\(_3\) catalysts. The reduction / oxidation of Mo is however not significantly influenced by the presence of steam (see Figures 4.6 and 4.14), which is in line with findings from experiments using ex situ X-ray photoelectron spectroscopy. H\(_2\)O adsorbs on the surface competitively to H\(_2\)S and C\(_4\)H\(_4\)S, in effect slowing down the desulfurization reactions.

4.5.3 Suitability of Mo catalysts for hot-gas sulfur removal

From the presented results, it is clear that Mo/Al\(_2\)O\(_3\) is a suitable catalyst for hot gas desulfurization. At 600 °C, all H\(_2\)S and C\(_4\)H\(_4\)S, which are used here as model compounds for sulfur species in producer gas, are removed under dry conditions. Over the 10 - 15 cycles under reducing and oxidizing atmosphere, the catalyst is stable, as indicated by stable levels of SO\(_2\) that is removed upon oxidation (see Figure 4.4), enabling long-term use for desulfurization. Adjustment of the residence time of the catalyst in the sulfur-containing producer gas will avoid the breakthrough of C\(_4\)H\(_4\)S.

Promotion of the catalyst with other metals, such as Co, can be an option to minimize the negative impact of steam. Comparison of unpromoted Mo/Al\(_2\)O\(_3\) catalyst with CoMo / Al\(_2\)O\(_3\) catalysts showed that the unpromoted catalyst was more prone to inhibition of hydrodeoxygenation by steam than the promoted one. On the other hand, promotion with Ni was found to enhance the negative effect of steam, due to oxidation of Ni sulfides. Therefore, dedicated materials development for improved desulfurization of producer gas must take the effect of water into account.
4.6 Conclusion

The suitability of Mo catalysts, supported on Al$_2$O$_3$, for hot-gas removal of sulfur in the absence and presence of steam was investigated. While the activity for sulfur removal was studied by mass spectrometry, the state of the molybdenum was probed by time resolved in situ X-ray absorption spectroscopy at the Mo K-edge. Experiments at 600 °C showed that under dry conditions, H$_2$S, which is the most abundant sulfur species in producer gas, and C$_4$H$_4$S, as model compound for organic sulfur species, are completely removed by Mo. The presence of steam is detrimental for removal of H$_2$S and C$_4$H$_4$S from the gas, due to competitive adsorption of steam on the Mo surface, blocking sites for sulfur adsorption.

Based on the measurements of reactivity and structure of the Mo catalyst, mechanisms for sulfur removal were proposed; H$_2$S is removed by sulfidation of MoO$_3$ to MoS$_2$ with concurrent reduction of MoO$_3$ to MoO$_2$. Removal of C$_4$H$_4$S occurs over MoO$_2$ by hydrogenolysis of C$_4$H$_4$S, forming MoS$_2$ and C1 - C4 species. This process however is slower than catalytic hydrogenation of C$_4$H$_4$S over MoS$_2$. Subsequent oxidation to SO$_2$ allows sequestration of the sulfur from the producer gas stream and regeneration of the catalyst.

Overall, this chapter shows that Mo based catalysts are excellent candidates for sulfur removal from biomass-derived gas at high temperatures, removing H$_2$S and organic sulfur compounds. This can improve the efficiency of catalytic biomass conversion.
Chapter 5

Integrated methane synthesis and sulfur removal over ruthenium based catalysts

5.1 Abstract

Catalytic conversion of natural feedstocks, such as wood, into synthetic natural gas (SNG) has large potential for sustainable energy supply. Sulfur, which is present in all biomass, needs to be removed from the gas to protect catalysts. Current technology using wet scrubbing to remove sulfur species between the gasification and catalytic conversion decreases the overall efficiency and therefore impedes commercialization. In this chapter it is shown that sulfur removal from the gas stream with integrated methane synthesis at high temperatures is possible over many cycles, using supported Ru catalysts. The sensitivity of X-ray absorption spectroscopy was improved by using a modulated excitation approach, showing that the catalyst is poisoned by sulfur and it can be fully regenerated. The proposed mechanism where sulfur is stored on the support and released under reducing conditions, leading to a re-poisoning of the catalyst, highlights the role of the support for sulfur poisoning and efficient regeneration. The integrated process of methanation and sulfur removal can make the biomass-to-SNG process more efficient by replacing wet scrubbing.

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The transmission electron micrographs of the sample in this chapter were supplied by Frank Krumeich at ETH Zürich, Jakub Szlachetko participated in fruitful discussions.
CHAPTER 5. METHANATION AND DESULFURIZATION OVER RU

5.2 Introduction

Dry biomass, such as wood, is a sustainable feedstock to partially replace fossil fuels, such as natural gas. Gasification of biomass, cleaning of the producer gas and subsequent methanation generates synthetic natural gas (SNG), which can be distributed in the existing gas grid. Gas cleaning is required after the gasification step, since biomass, like coal, contains significant amounts of sulfur, that form compounds such as $\text{H}_2\text{S}$, $\text{COS}$ or $\text{C}_4\text{H}_4\text{S}$ upon gasification, which are known to poison the methanation catalyst. For this process to be cost-effective, it needs to be energy efficient. Currently, gas cleaning is done after the high temperature gasification step by low temperature scrubbers, causing water condensation, while the gas needs to be heated above 300 °C afterwards, for catalytic methanation. Techno-economic analysis of a biomass to ethanol process showed that current technology for gas cleaning (tar reforming, acid gas and sulfur removal) represents 31% of the minimum selling price of the produced ethanol. Improving the gas cleaning efficiency is therefore essential to make biomass-derived fuels more competitive. Mid- to high-temperature sulfur cleaning processes have been proposed to overcome energy inefficient scrubbing, which are either primary sulfur removal by adding a sorbent to the gasifier, or secondary cleaning, by a dedicated reactor between the gasifier and the methanation reactor. The proposed high-temperature gas cleaning processes so far only concern removal of $\text{H}_2\text{S}$, while organic sulfur compounds, such as thiophenes, are usually not tested.

If the sulfur removal step is not complete or fully omitted, the challenge is to regenerate sulfur poisoned methanation catalysts, of which Ni-based catalysts are mostly used commercially. Regeneration can be performed under reductive, oxidative, steam or inert environment. Oxidative regeneration, typically in air or in an air / flue gas mixture, has been shown to quickly remove large amounts of sulfur. However, oxidation of Ni catalysts poisoned with S forms NiSO$_4$, which is stable up to $\sim$ 800 °C. Regeneration at these temperatures is not only costly, but also leads to irreversible sintering of catalyst nanoparticles, and therefore to loss of activity.

Ruthenium based catalysts are also known to be good methanation catalysts. In contrast to Ni, stability diagrams show that Ru-based catalysts do not form sulfates upon oxidation. This is shown in Figure, where the dominant phases for the Ni-S-O and the Ru-S-O systems are shown for a constant temperature of 600 °C. While Ni forms a NiSO$_4$ sulfate in a relevant range of parameters, Ru does not form a sulfate phase.

This suggests that regeneration of Ru catalysts by $\text{O}_2$ is feasible. The efficiency of the overall wood to SNG process is expected to be significantly improved by directing the gas stream from the gasifier directly over the methanation catalyst and thus skipping the low temperature gas cleaning step. In this chapter, the integration of methane synthesis with sulfur removal is explored. The poisoned Ru catalyst is regenerated in oxidative atmosphere, while the mechanisms
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Figure 5.1: Calculated phase diagrams for the Ni-S-O system (left) and the Ru-S-O system (right) at 600 °C. Displayed are the dominant phases as a function of $p_{SO_2}$ and $p_{O_2}$.

for poisoning and regeneration of the methanation catalyst are followed in situ using modulated excitation XAS.
5.3 Materials and methods

5.3.1 Catalyst

The Ru/Al₂O₃ (2 wt-% Ru) catalyst was prepared by wet-impregnation of Ru³⁺ nitrosyl nitrate solution (Aldrich), and was calcined at 500 °C. Figure (5.2) shows transmission electron microscopy (TEM) images of the fresh catalyst sample, indicating a particle size of 10 - 30 nm.

Figure 5.2: TEM micrographs of the catalyst in bright-field (BF) mode (left) and Z-contrast (ZC) mode (right). The spots which appear dark in BF mode and bright in ZC mode are Ru nanoparticles, as confirmed by EDX.

5.3.2 In situ experiments

In situ methanation, poisoning and regeneration experiments were conducted in a capillary reactor. The total cycle time was 1800 seconds for the non-isothermal experiments and 1200 seconds for the isothermal experiments, the total flow rate was always kept at 20 ml min⁻¹. Prior to the poisoning/regeneration experiments, identical experiments were performed without sulfur, and without sulfur and CO, respectively. The plug flow microreactor (quartz capillary with 2.8 mm ID, 3.0 mm OD) was filled with ca 15 mg of the catalyst, kept in place by plugs of quartz wool.

The experimental setup was similar to the one used in the previous chapters. The reactor was heated by a hot air blower, the temperature was measured with a thermocouple inside the reactor. The pressure in the reactor was kept at 0.5 bar overpressure by a pressure-controlling valve. The temperatures during the methanation and poisoning (Tₚ) and the temperature during the regeneration period (Tᵣ) were varied between 300 °C and 600 °C or all kept at 430 °C. During heating, the catalyst was flushed with He (quality 4.6). The gas composition at the inlet and the outlet of the reactor was measured with a quadrupole mass spectrometer (Extrel, USA). The gas composition at the reactor inlet was varied according to the following scheme:
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1. 120 s $\text{H}_2$ (2.5 %) in $\text{He}$
2. 240 s $\text{H}_2$ (2.5 %), $\text{CO}$ (0.25 %) in $\text{He}$
3. 300 s $\text{H}_2$ (2.5 %), $\text{CO}$ (0.25 %), $\text{H}_2\text{S}$ (60ppm), $\text{COS}$ (6 ppm), $\text{C}_4\text{H}_4\text{S}$ (12 ppm) (in Ar)
4. 120 s - 360 s He flushing
5. 360 s - 420 s $\text{O}_2$ (0.25 %) in $\text{He}$
6. 60 s - 360 s He flushing

For the isothermal experiments, the He flushing was 120 s and 60 s before and after the 360 s lasting oxidation, respectively. For the experiments where the oxidation was performed at elevated temperatures for 420 s, the flushing duration was 360 s before and after oxidation to allow for heating and cooling.

5.3.3 Offline experiments

To verify the in situ experiments and to reach higher levels of sulfur exposure in a reactor with more homogeneous temperature distribution, reactivity experiments were performed offline (i.e. without X-ray beam) in a steel tube reactor with 1/4 inch outer diameter, which was sulfinert coated to prevent sulfur adsorption in the tube (Restek). The sequence of gas exposure was similar to the one described above, only with longer exposure to sulfur, higher $\text{H}_2$, $\text{CO}$ and $\text{O}_2$ concentrations, and $\text{N}_2$ added during the regeneration period, to simulate regeneration with air or diluted air. The detailed conditions were as follows:

1. 120 s $\text{H}_2$ (33.3 %) in $\text{He}$
2. 300 s $\text{H}_2$ (33.3 %), $\text{CO}$ (6.7 %) in $\text{He}$
3. 840 s $\text{H}_2$ (33.3 %), $\text{CO}$ (6.7 %), $\text{H}_2\text{S}$ (60 ppm), $\text{COS}$ (6 ppm), $\text{C}_4\text{H}_4\text{S}$ (12 ppm) (in Ar)
4. 180 s He flushing
5. 180 s $\text{O}_2$ (5 %), $\text{N}_2$ (17 %) in $\text{He}$
6. 180 s He flushing

The catalyst was identical to the one used in the XAS experiments, of which $\sim$ 75 mg were used. The temperature was set to 430 °C, the pressure was 2 bar absolute during all offline experiments.

5.3.4 XAS setup

Ru K-edge quick XAS spectra of the supported Ru catalyst were acquired at the SuperXAS beamline at the Swiss Light Source in transmission mode. The X-ray beam from the bending
magnet was monochromatized with a Si(111) channel-cut crystal in the QuickXAS monochromator. The Si(111) crystal was rotated at a frequency of 0.2 Hz around the Ru K-edge (22117 eV) and the signals of the ionization chambers and the angular encoder were sampled with 2 kHz. The edge energy was calibrated by a Ru foil after the sample.

5.3.5 Generalized method for the demodulation of data with more than 2 states and non-equidistant excitation

As explained in chapter (2), modulated excitation spectroscopy describes a method where a sample (e.g. a catalyst) is periodically excited by an external stimulation, such as a change in gas atmosphere, and the state of the sample is measured by time-resolved spectroscopy. [71] The measured data is then filtered with the known excitation frequency, removing contributions to the signal that either occur at lower frequencies (i.e. static species), or at higher frequencies (i.e. noise). This procedure is called demodulation or phase-sensitive detection, and it generates difference spectra between the different states that follow the excitation with a significantly improved signal to noise ratio. Modulated excitation XAS was recently introduced as a method to increase sensitivity of XAS to small changes in a sample’s state. [77, 79] We developed a method for quantitative analysis of the data for cases with two equidistant discrete states (see chapter 2). So far, the theory for modulated excitation XAS was only formulated for experiments with two states that exist equally long. In this chapter, a way of analyzing demodulated data is proposed where the signal changes in two steps which do not necessarily last for the same time. As will be shown, this concept is not limited to two step functions, but generally valid for periodic functions, and is also applicable to XAS data. However, for the sake of clarity and simplicity, it is discussed here only for two step functions.

The demodulation formula is: [71]

$$A_k^{PSD}(E) = \frac{2}{T} \int_0^T A(E, t) \sin(k \omega t + \Phi_{PSD}) dt$$ (5.1)

The demodulation procedure is essentially a Fourier filtering of an original signal $A(E,t)$ with a periodicity $T$ and a frequency $\omega = \frac{2\pi}{T}$, which is transformed from the time-domain into the phase-domain with the phase $\Phi_{PSD}$. In the following, we only consider the case of the fundamental frequency where $k = 1$. The resulting demodulated signal can be regarded as a difference spectrum which contains only those changes in the sample’s state that occur as a result of the modulated excitation. Compared to differences of full spectra, data quality (i.e. signal to noise ratio) in demodulated spectra is higher, because noise is largely removed. [67, 79] If the sample’s structure changes through one or more intermediate states, the demodulated spectra will show the transitions between the different states.

In the experiments in this chapter, Ru particles were exposed to three different conditions:
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reducing (in H₂ and CO, i.e. methanation), reducing and sulfiding (in H₂, CO and H₂S) and oxidizing (in O₂). For the isothermal experiment, the three regimes last for 360 s, 420 s and 420 s, respectively. The three states cannot be clearly distinguished in the XAS signal, since the XAS signal is a wave function, rather than a peak (such as IR or XRD).

If the original signal (i.e. the XAS spectrum) can be deconvoluted into two different signals, the demodulation can be performed on those two different signals. The sum of these two de-modulated functions will again be the same as the demodulated function of the original signal. This is demonstrated in the following. Consider a time-dependent signal A(t) which takes three discrete values. It can be deconvoluted into two step functions A₁(t) and A₂(t).

\[ A(t) = A_1(t) + A_2(t) \]

A₁(t) and A₂(t) are periodic step functions with a period length T which can be described by a step height (h₁ = H₁ - H₀, h₂ = H₂ - H₀), the time of the step (S₁, S₂), and the duration of the step (D₁, D₂) (see Figure (5.3)),

\[ A_i(t) = H_0(t < S_i; t > S_i + D_i)H_i(S_i < t < S_i + D_i) \]

Where \( i = 1, 2, 0 < t < T \)

The periodic step function A_i(t) can be expressed as a Fourier series

\[ A_i(t) = H_0T + D_ih_i + \frac{h_i}{k\pi} \sum_{k=1}^{\infty} (a_k \cos(k\omega t) + b_k \sin(k\omega t)) \]

with the Fourier coefficients \( a_k = (\sin((d + s)k) - \sin(sk)) \) and \( b_k = \cos(sk) - \cos((d + s)k) \)

where \( d = 2\pi D/T, s = 2\pi S/T \) and \( T = 2\pi/\omega \). Note that \( a_k \) and \( b_k \) only depend on the time when the step function starts (s) and its duration (d). These values can therefore be predicted by the known excitation start and duration of the system, or can be approximated based on additional knowledge, if the system’s response is not instantaneous. When the demodulation procedure is performed on A_i(t), the resulting demodulated function for \( k=1 \) is:

\[ A_k^\phi = \frac{2}{T} \frac{h_i}{\pi} (a_k \int_0^T \cos(\omega t) \sin(\omega t + \phi) dt + b_k \int_0^T \sin(\omega t) \sin(\omega t + \phi) dt) = \]

\[ = \frac{2}{T} \frac{h_i}{\pi} (a_k \pi \sin(\phi) + b_k \pi \cos(\phi)) = \]

\[ = \frac{2h_i}{T} (a_k \sin(\phi) + b_k \cos(\phi)) \]

The relation between the amplitude of the demodulated spectrum (\( A^\phi \)) and the amplitude change of the original function (h) at a given phase angle can therefore be calculated solely based on the
Fourier coefficients $a$ and $b$, which in turn can be derived from the known values for the duration of a state ($D$), its starting time ($S$) and the period length ($T$). This allows correct scaling of the demodulated spectra, so that they can be fitted as regular difference spectra (see chapter (2)).

Furthermore, the demodulated spectra of a signal which contains more than one step function will simply be the sum of the individual demodulated spectra of each step function. If the steps are phase shifted, the corresponding demodulated spectra will be too. At certain phase angles, one contribution will therefore be zero, while the other one is non-zero, effectively isolating the two contributions to the overall signal from each other. This allows detection of small changes in the spectra, as will be discussed in the following.

To show how this works in practice, a simple example is given in which the following periodic function is considered, with a period length of 1200 s, as in the data for the isothermal experiment:

$$A(t) = \begin{cases} 0 & : t < 360s \\ 0.1 & : 360s \leq t < 780s \\ 1 & : 780s \leq t < 1200s \end{cases}$$

This signal $A(t)$ can be deconvoluted in two step functions, $A_1(t)$ and $A_2(t)$ so that $s_1 = 0.6\pi, h_1 = 0.1, d_1 = 0.7\pi$ and $s_2 = 1.3\pi, h_2 = 1, d_2 = 0.7\pi$ as is shown in Figure (5.3a).

The Fourier coefficients for $A_1$ are:

$$a_1 = -1.760, b_1 = 0.289$$

For $A_2$:

$$a_1 = 0.809, b_1 = -1.588$$

The demodulated function of $A_1$ for $k = 1$ is therefore:

$$A_{1\phi} \approx -0.056sin(\phi) + 0.009cos(\phi)$$

For $A_2$:

$$A_{2\phi} \approx 0.258sin(\phi) - 0.505cos(\phi)$$

And the demodulated function for $A$ is the sum of the two individual demodulated functions:

$$A_{\phi} \approx 0.202sin(\phi) - 0.496cos(\phi)$$

Figure (5.3b) shows the resulting demodulated functions for $A_1, A_2$ and $A$. The two functions, $A_1$ and $A_2$ are phase shifted, so that while $A_2$ is zero, the amplitude of $A_1$ is about 80% of its maximum.

For the demodulation of XAS spectra which are a convolution of two subsequent changes (e.g. formation of a minor Ru-S contribution and the formation of a major Ru-O contribution), this
Figure 5.3: Demodulation of a two-step function. a) The original signal A can be deconvoluted into two step functions A1 and A2. b) resulting demodulated functions of the original signal and its components A1 and A2.

means that the minor contribution can be ideally detected around the phase angle at which the major contribution passes through zero. Since the major contribution dominates the overall signal, this will be close to the phase angle at which the observable overall function passes through zero. If the points in time at which the two steps occur (i.e. the excitation by feeding H2S or O2) are known, the phase angles of the two contributions in phase space (A1 and A2) can be calculated, along with the ratio of amplitudes of the known demodulated spectrum and the unknown difference spectrum. This in turn allows correlating the information of the demodulated spectra, and the original data in a quantitative way, which is a prerequisite for EXAFS fitting. If the points in time are not exactly known, but can be estimated (e.g. from another analysis method, such as mass spectrometry), the resulting values are still close to the original values.

5.3.6 EXAFS data analysis

The Ru-Ru peak of full Ru K-edge spectra was fitted in k2-weighting over a range from 1.5 - 3 Å in R-space and 3-13 Å\(^{-1}\) in k-space, using the IFEFFIT software suite. [62] First, the
full spectrum of the reduced state was fitted as a reference for the demodulated spectra. The amplitude reduction factor $S_0^2$ was set to 0.87, as extracted from fitting of a Ru metal foil. Demodulated spectra at $\phi = 234^\circ$ and $124^\circ$ were analyzed according to our method described in detail in chapter 2. Briefly, the fitting of demodulated spectra is done as follows: First, the spectra are scaled with a factor that is derived from the Fourier analysis of the excitation step functions (see section 5.3.5) to match the amplitude of the difference spectra. The fitting is done with a model that includes both states of the sample, where the first state corresponds to the previously fitted reference. In the present case, the Ru-Ru (Ru$^0$) shell was used twice, where the first one used the parameters extracted from the fit of the full spectrum of the reduced catalyst. The second Ru-Ru shell was floating free, and was fitted over an R-range of 2-3 Å. Subsequently, the parameters of these two Ru-Ru paths were fixed, and the minority species was fitted over an R-range of 1-3 Å. For the demodulated spectrum with $\phi = 234^\circ$, a Ru-S shell was used as minority species, since the spectrum at this phase angle contains only the transition from the active to the poisoned catalyst. For the demodulated spectrum with $\phi = 124^\circ$, a Ru-O shell was used as minority species, representing the transition from fully reduced to partially oxidized catalyst. All paths used the $E_0$ determined from fitting of the full spectrum. The demodulated spectra were fitted over a k-range from 3-12 Å$^{-1}$ and 3-14 Å$^{-1}$ for the transition active state - poisoned state and the transition poisoned state - oxidized state, respectively.
5.4 Results and discussion

In the proposed integrated process, the methanation catalyst would be poisoned over time by the sulfur species in the producer gas from the gasifier and subsequently regenerated in an oxygen-containing gas stream. This could be realized in a swing-reactor design, or a dual fluidized bed, similar to chemical looping reactors. The changes in the catalyst’s state while it undergoes transient conditions of methanation, poisoning and regeneration are tracked by time-resolved X-ray absorption spectroscopy. Periodic, reproducible changes in the catalyst’s state allow extracting the structure of only the changing atoms using modulated excitation XAS, which increases the sensitivity (see chapter (2)).

5.4.1 Non-isothermal conditions

To simulate the exposure of a Ru catalyst to the varying gas concentrations (sulfur-containing producer gas and diluted O₂, respectively) and temperatures in this process, the gas feed and temperatures of the fixed-bed micro reactor were modulated (Figure (5.4)). A gas stream that is similar to one from a biomass gasifier (H₂, CO, H₂S, COS, C₄H₄S) was fed to the reactor containing ∼15 mg of Ru/Al₂O₃ (2 wt-% Ru) catalyst at a total flow rate of 20 ml·min⁻¹, while the temperature for methane synthesis (Tₐ) was kept at 300 °C, and the regeneration temperature (T_r) was initially set to 550 °C, and was then lowered stepwise.

Catalyst activity

Gas analysis at the reactor outlet shows that the catalyst is deactivated by sulfur, and its activity is restored by oxidative regeneration. At time t₁ (see Figure (5.4)), H₂ is flowing through the reactor, reducing the catalyst. Upon addition of CO to the H₂ flow (time t₂), CH₄ is produced. Sulfur is added to the gas mixture at time t₃. Approximately 110 seconds after addition of the sulfur species at time t₃, C₄H₄S is detected at the reactor outlet, while simultaneously the methane signal decreases, indicating loss of catalyst activity. When the catalyst is heated to 550 °C and oxidized with diluted O₂ (time t₅), SO₂ (m/z 64) is released. In the next cycle, the methanation activity is recovered and the sequence is repeated. Figure (5.4) shows that this process can be repeated 20 times with approximately 50 % decreased methanation activity at the end of 20 cycles, as measured by integrating the CH₄ signal (m/z 15) over each cycle. The amount of SO₂ that is released from the reactor rises from the 1st to the 20th cycle. This suggests that sulfur accumulates in the system, and cannot be fully removed within one regeneration cycle. The regeneration product SO₂ is likely to adsorb to the catalyst particles downstream in the reactor, as SO₂ is known to react with Al₂O₃. In the next regeneration sequence, this sulfur is partially released together with the freshly deposited sulfur, increasing the total amount of SO₂ that is measured at the outlet.
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Figure 5.4: Nominal gas flows (top) and temperature profile (middle) during one cycle of methanation and poisoning (He was used for flushing and to balance to 20 ml $\cdot$ min$^{-1}$). Mass spectrometer traces (bottom) for the reactor outlet of the non-isothermal experiment where methanation was performed at 300 °C and regeneration was performed at 550 °C. Shown are $\text{CH}_4$ (m/z 15, black), $\text{C}_4\text{H}_8\text{S}$ (m/z 84, blue) and $\text{SO}_2$ (m/z 64, red). The solid lines show the first cycle, the dashed lines the 20th cycle. The vertical dashed lines indicate times where gas flows were changed, as referred to in the text.

In situ XAS spectra

Time-resolved X-ray absorption spectra were taken in situ, showing that the catalyst is in the metallic state during methanation, and largely oxidized to RuO$_2$ upon regeneration. The Fourier transform of the active catalyst in Figure 5.5 shows that the structure is that of metallic Ru, showing no signs of bulk sulfidation. The spectrum was taken at the beginning of the methanation sequence at 300 °C, after regeneration at $\sim 475$ °C, after 29 cycles of poisoning and regeneration with a regeneration temperature of $\sim 550$ °C, and further 3 cycles at a regeneration temperature of $\sim 500$ °C.
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5.4.2 Isothermal conditions

Changing the temperature between methanation and regeneration in a full-size plant increases operational complexity and adds thermal stress to the catalyst. Therefore isothermal operation (i.e. performing methanation and regeneration at the same temperature) is desired. While low temperatures are favorable for full CO conversion, higher temperatures facilitate breaking the metal-sulfur bond. The regeneration temperature $T_r$ was lowered in steps while monitoring the effect of these temperature changes on the activity and regeneration.

Catalyst activity

At $T_r \sim 430 \, ^\circ C$, regeneration was still satisfactory. In a next step, $T_m$ was increased to 430 °C for isothermal operation with a fresh catalyst sample. Figure 5.6 shows the mass spectrometer traces of the first and the 20th cycle for the experiment where the temperature in the reactor was kept at 430 °C. The SO$_2$ output upon regeneration is significantly lower, which indicates that less sulfur is removed from the catalyst, compared to the non-isothermal experiment (see Figure 5.4). Most importantly, the total amount of CH$_4$ produced during the 20th cycle is significantly lower than during the first, indicating faster deactivation. Experiments at 430 °C represents a trade-off between formation of strongly bound RuS$_2$ at higher temperatures and insufficient regeneration at lower temperatures, while still being thermodynamically favorable for high CO conversion, thereby potentially eliminating the need for a secondary methanation reactor. Moreover, operating methanation and regeneration at the same temperature facilitates the process.

Additional offline experiments (i.e. without simultaneous XAS) at 430 °C confirmed that a
steady state can be reached, where the total amount of methane produced per cycle remains constant, thus allowing continuous operation of the integrated methane synthesis and sulfur removal reactor. Figure (5.7A) shows the MS traces of selected masses for the 1st and 13th cycle of the methanation, poisoning and regeneration. While the methanation activity is not affected by sulfur poisoning during the first cycle, because the catalyst load is higher than needed for full conversion, the catalyst severely deactivates during the 13th cycle.

Again, while the CH$_4$ signal drops, the C$_4$H$_4$S signal rises, showing the breakthrough of sulfur until all of the catalyst is poisoned. Furthermore, even before addition of sulfur to the feed, CH$_4$ production drops, indicating a spillover of sulfur from the catalyst support. Figure (5.7B) shows the integrated methane output per cycle before addition of sulfur to the feed, during sulfur addition, and after sulfur was again removed from the feed. When sulfur was removed from the feed, methane production increased to $\sim 65\%$ of the initial level under sulfur-free conditions.

**In situ XAS spectra**

To obtain an insight in the poisoning mechanism and regeneration mechanism, X-ray absorption spectroscopy (XAS) was applied in situ. Three representative experimental XAS spectra of the catalyst in the reduced, active state at 100 s (black), in the sulfur-poisoned state at 700 s (blue) and the partially oxidized state at 1000 s (red) are shown in Figure (5.8) for the isothermal experiment at 430 °C. The inset shows the evolution of the absorption coefficient at 22.133 keV, where the difference in absorption coefficient is largest, over time. At 800 seconds, the catalyst is oxidized, which leads to an increase in absorption at this energy. However, the effect of sulfur...
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Figure 5.7: A) selected MS traces for the 1st (solid lines) and 13th (dashed lines) cycle of the offline experiments. B) CH$_4$ production per cycle over multiple cycles for the isothermal experiment at 430 °C under sulfur-free conditions, with sulfur added and again under sulfur-free conditions.

poisoning, which should occur between the spectra at 100 s and 700 s, is not visible in the full spectra, nor in the temporal evolution.

Since S poisoning largely affects the surface, detecting sulfur poisoning of catalysts in situ is challenging, especially for large Ru particles that were used in this study (10 - 30 nm, as determined by scanning transmission electron microscopy, see Figure 5.2). To increase the sensitivity to the fraction of Ru atoms that changes its local structure upon poisoning and regeneration, a modulated excitation approach was employed, in which an experimental parameter (gas partial pressure and/or temperature) is exciting the system, and is modulated periodically. Filtering of the measured system response, i.e. the XAS spectra, with the known excitation frequency keeps the XAS signal of only the atoms that change, while removing static
signals and noise. This leads to a significantly improved sensitivity with respect to small changes. The resulting demodulated spectra were fitted based on the fitting approach developed in chapter 2. The fitting scheme was further generalized for cases where the reaction goes through an intermediate, and where the excitation has arbitrary shape (see section 5.3.5). This allows for the first time detection and quantification of minor species under complex experimental conditions with multiple changes in the sample’s state.

In Figure (5.8A) the EXAFS signals of two full spectra in Figure (5.8) are extracted and the difference spectrum is shown, together with demodulated spectra at phase angles between 10 and 350°. The demodulated spectra basically show the same information as the difference spectrum, only with improved signal to noise (S/N) ratio. The difference spectrum in Figure (5.8A) shows the difference between the active, reduced state, and the partially oxidized state. The demodulated spectra are expected to have two contributions: the transition from active to poisoned Ru (i.e. the formation of Ru-S bonds), and the transition from poisoned catalyst to partially oxidized catalyst (i.e. the formation of Ru-O bonds and simultaneous breaking of Ru-S bonds). Since the oxidation is already clearly visible in the full spectra (Figure (5.8)), it is expected to dominate the demodulated spectra, while the contribution from the Ru-S formation is expected to be minor. The demodulated spectra are a convolution of the two processes, which are shifted relative to each other in time, and therefore in phase, such as described in section 5.3.5.

In order to deconvolute the two contributions (formation of Ru-S and formation of Ru-O), we can select the demodulated spectrum at the specific phase angle, at which the signal of the dominant contribution (the formation of Ru-O) passes through zero. One such point for the dominant contribution is 4.85 Å⁻¹ (indicated in Figure (5.9A) by the vertical dashed line). The
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Figure 5.9: a: EXAFS signal in k-space (k^2-weighting) of full spectra, showing the reduced and the partially oxidized state, the difference spectrum, and demodulated spectra at phase angles between 10° and 350°. b: signal amplitude (k^2-weighting) versus phase angle for the demodulated spectra at k = 4.85 Å\(^{-1}\) as indicated by the dashed line in (A).

Evolution of the signal of the demodulated spectra over the phase angle at a fixed value of 4.85 Å\(^{-1}\) is plotted in Figure (5.9B). It is found that this signal passes through zero at phase angles of 54° and 234°.

If there is a contribution other than the dominant Ru-O phase to the demodulated spectra, it would most likely show up at phase angles around 54° and 234°. In Figure (5.10), single demodulated spectra at phase angles between 231° and 239° are compared to a demodulated spectrum at 310°, which has the highest amplitude of the demodulated spectra. The overall shape of the spectra around 234° is significantly different than the one at 310°. In addition, at some k-values (e.g. 2.5 Å\(^{-1}\), 3 Å\(^{-1}\), 4.8 Å\(^{-1}\), 5.7 Å\(^{-1}\), 8.25 Å\(^{-1}\), 8.95 Å\(^{-1}\), indicated by the solid vertical lines) the signal changes strongly over the 9° while for other k-values, the signal...
changes only very little (4.35 Å⁻¹, 5.35 Å⁻¹, 6.5 Å⁻¹, dashed vertical lines). The peaks of the first type can therefore be ascribed to the major contribution (e.g. function A2 in Figure [5.3]), which is going through the highest gradient, while the latter ones can be ascribed to the minor contribution, which is going through a maximum, and therefore has a small gradient (see Figure [5.3]B, where A2 goes through zero with a high gradient, while A1 is almost at maximum amplitude with a small gradient)

Figure 5.10: EXAFS signal in k-space (k²-weighting). Single demodulated spectra at phase angles of 231°, 233°, 235°, 237°and 239°(top) and at a phase angle of 310°(bottom). The solid vertical lines indicate peaks of the demodulated spectrum at 310° which represent the major contribution, while the dashed vertical lines indicate peaks of the second minor contribution.

In comparison to the experiment with sulfur (Figure [5.10]), the demodulated spectra of the experiment without sulfur (i.e. only methanation and oxidation) in Figure [5.11] show a very similar shape for the demodulated spectrum at 310° which is ascribed to the major contribution of the Ru oxidation. At phase angles around 235° however, the spectra look quite different, and there is one phase angle (233°, indicated by the red line), at which the whole spectrum shows no peak. This corroborates the notion that the spectra of the experiment with sulfur do indeed consist of two contributions which are phase shifted to each other, while the spectra of the experiment without sulfur only contain one contribution. Therefore the minor contribution is likely to be due to formation of Ru-S.

For EXAFS fitting, the demodulated spectra need to be scaled correctly, so that their amplitude is equal to that of the original difference spectra. In the case of the major Ru-O contribution, this can be easily done by scaling a demodulated spectrum to the difference spectrum shown in Figure [5.9]. For the minor contributions, this needs to be done analytically, by using the expressions derived above. For the minor contribution (formation of Ru-S) occurring at 360 s < t < 780 s, the Fourier coefficients are \( a_1 = -1.760 \) and \( b_1 = 0.289 \). At a phase angle 235° we find:
5.4. RESULTS AND DISCUSSION

Figure 5.11: EXAFS signal ($k^2$ weighted) of selected demodulated spectra for the experiment without sulfur. The spectrum at 233° is indicated in red.

\[ A_k^\phi = \frac{2h_1}{T}(a_k \sin(\phi) + b_k \cos(\phi)) = 0.406 \cdot h_i \]

The signal amplitude at 235° needs therefore to be divided by 0.406 in order to obtain the difference in the original signal $h_i$. For the major contribution at 780 s $t$, the Fourier coefficients are $a_1 = 0.809$ and $b_1 = -1.588$. At a phase angle 190° where the demodulated signal of the minor contribution goes through zero (Figure (5.3)), we find that the signal of the major contribution needs to be divided by 0.453 to obtain the original signal.

The resulting Fourier transforms of the catalyst in active, poisoned and regenerated state are shown in Figure (5.12), where the active state is based on the full XAS spectrum, while the poisoned and regenerated states were derived from the demodulated spectra.

The full XAS spectra show the first Ru-Ru coordination shell of metallic Ru at 2.67 Å for the active catalyst, and additionally the first Ru-O coordination shell of RuO$_2$ at 1.8 Å for the oxidized catalyst. Fitting of these functions gives the structural parameters as shown in Table (5.1).

The transition from the reduced, active catalyst to a poisoned catalyst happens 2-3 minutes after the sulfur species are added to the gas flow. The Fourier transform of the corresponding demodulated XAS spectrum shows that at that time a Ru-S bond appears at 2.299 Å, as shown in Figure (5.12). Fitting yields a coordination number of 0.07 for the Ru-S bond. This indicates that, with an estimated dispersion (ratio of number of surface atoms to total number of atoms) of 0.1, 70% of surface Ru atoms are poisoned by S. When the poisoned catalyst is subsequently oxidized with 0.25 % O$_2$ in He, the Ru-Ru coordination number decreases, while a Ru-O shell with a coordination number of 1.4 appears at 1.932 Å, indicating that $\sim 23$ % of Ru is oxidized.
The demodulated XAS spectra which indicate the transition between active and poisoned state showed no significant differences between the experiment where the temperature for methane synthesis $T_m = 300 \, ^\circ\text{C}$ and the regeneration temperature $T_r = 600 \, ^\circ\text{C}$, and the experiment where $T_m = T_r = 430 \, ^\circ\text{C}$. Analysis of the demodulated spectra at the same phase angle from different periods of the isothermal process at $300 \, ^\circ\text{C}$ are similar to those of the isothermal process at $430 \, ^\circ\text{C}$, indicating that the state of the sulfur-poisoned catalyst is similar, independent of poisoning temperature, and independent of the number of regeneration cycles. This suggests that sulfur can be removed from the Ru catalyst during each regeneration step, but accumulates somewhere in the catalyst bed during each poisoning cycle. The progressing poisoning from cycle to cycle is most likely an effect of the support, which stores sulfur, e.g. by forming $\text{Al}_2(\text{SO}_4)_3$, which subsequently spills over to the Ru catalyst upon reduction of the $\text{Al}_2(\text{SO}_4)_3$ to $\text{Al}_2\text{O}_3$, $\text{SO}_2$ and $\text{H}_2\text{O}$, leading to poisoning of the catalyst even in the absence of sulfur in the gas feed. This is supported by the fact that after complete deactivation and subsequent regeneration, the sulfur-free feed leads to methanation activity, which again drops quickly, even before adding sulfur to the feed (see Figure 5.7). While $\text{H}_2\text{S}$ and $\text{SO}_2$ were shown to physisorb on the OH surface groups of $\text{Al}_2\text{O}_3$, Yoo et al. observed by X-ray diffraction that $\text{Al}_2\text{O}_3$ is...
5.4. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>t = 100 s</th>
<th>Ru-Ru</th>
<th>CN</th>
<th>R / Å</th>
<th>DW / Å²</th>
<th>E₀ / eV</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>11.9</td>
<td>4.663</td>
<td>0.0088</td>
<td>-5.71 ± 1.72</td>
<td>0.046</td>
</tr>
<tr>
<td>±2.1</td>
<td>±0.010</td>
<td>±0.0015</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 234 °    | Ru-Ru | 11.9 | 2.674  | 0.0100  | -5.71 (set) | 0.027    |
|          |       | ±0.1 | ±0.015 | ±0.0023 |         |          |

| 234 °    | Ru-S  | 0.07 | 2.299  | 0.0040  | -5.71 (set) | 0.027    |
|          |       | ±0.02| ±0.012 | ±0.0030 |         |          |

| 124 °    | Ru-Ru | 8.3  | 2.664  | 0.0098  | -5.71 (set) | 0.034    |
|          |       | ±0.4 | ±0.002 | ±0.0004 |         |          |

| 124 °    | Ru-O  | 1.4  | 1.932  | 0.0050  | -5.71 (set) | 0.027    |
|          |       | ±0.2 | ±0.008 | ±0.0020 |         |          |

Table 5.1: Results of the EXAFS fitting of spectra representing the active, poisoned and the regenerated state as shown in Figure (5.12).

Sulfated into Al₂(SO₄)₃ by SO₂ at 500 °C, and that upon reduction with H₂, Al₂O₃ is formed again. Accordingly, we hypothesize that H₂S from the feed gas and SO₂ from the oxidation of RuSₓ adsorb on Al₂O₃, and subsequent oxidation forms Al₂(SO₄)₃. The following reductive phase partially reduces the sulfur to H₂S, which is released as gas poisoning the Ru catalyst downstream. The decomposition of the aluminum sulfate at high temperatures could cause the improved catalyst regeneration during the non-isothermal experiments.
5.5 Conclusion

The combination of mass spectrometry data and modulated excitation XAS data allows concluding that the poisoning of the catalyst is due to the formation of a surface RuS$_2$ phase, which is inactive for methanation. A general method for quantification of demodulated XAS spectra allowed highly sensitive detection of the minor ruthenium sulfide phase, which is not possible with regular EXAFS analysis. This methodology is generally applicable and also of interest for other in situ experiments where periodic modulations of the sample’s environment lead to small changes in its state.

Upon oxidation, SO$_2$, RuO$_2$ and Al$_2$(SO$_4$)$_3$ are formed. Subsequent reduction reactivates the catalyst and releases sulfur from the support. This mechanism is illustrated in Figure 5.13. The release of sulfur from the support under methanation conditions leads to subsequent poisoning of Ru particles downstream in the catalyst bed.

![Figure 5.13: schematic representation of the proposed processes of poisoning, regeneration and reactivation.](image)

Despite its high cost, it is shown in this chapter that Ru is an attractive catalyst for syngas methanation in the presence of sulfur, since it can be regenerated with a relatively easy process.
As Ru does not form a sulfate phase in the range of used operating conditions, it can be oxidized with rather high partial pressures of oxygen, allowing fast regeneration. The oxidative treatment will also remove possible carbon deposits, which is typically also a challenge for methanation of gasified biomass. Further optimization of the regeneration procedure presented herein, for instance by specific development of sulfur inert catalyst supports, can enable combined methanation and high temperature sulfur removal, removing the need for low temperature scrubbing. This would make conversion of biomass (or coal) to methane more efficient, and therefore more competitive.
Chapter 6

Probing the effect of the support on sulfur-poisoning using sulfur K-edge XAS

6.1 Abstract

Many catalyst supports are known not to be inert, but can react with certain molecules, such as sulfur species. Understanding the interaction of sulfur species with the supports is necessary to design improved catalysts or optimize regeneration protocols. In this study, we investigated the oxidation state of sulfur on two supported catalysts (Ru/Al₂O₃ and Ru/C) and blank supports under reaction conditions by X-ray absorption spectroscopy (XAS) at the sulfur K-edge. The two tested catalysts are active for the methanation reaction \(3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}\), and are sensitive to sulfur poisoning. It was found that Al₂O₃ supported Ru forms Ru-sulfides and sulfates on the support during poisoning. Upon regeneration, sulfur is transported from the Ru to the support, and is transported back upon subsequent reducing conditions, impeding complete regeneration. On C supported Ru, not all sulfur is removed by oxidation, making regeneration by oxidation impossible under the tested conditions.

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The Ru/Al₂O₃ sample was provided by Thanh-Bin Truong at PSI, the sulfur uptake measurements were performed by Patrick Schuh from the Technische Universität München.
6.2 Introduction

While heterogeneous catalysis is usually described in terms of the interaction between the re-
actants (gaseous or liquid) and the solid catalyst (often a metal, metal oxide or metal sulfide),
it is known that the catalyst support has an influence on the reaction. The support, such as a
porous oxide structure, highly crystalline zeolites, or active carbon, can influence the reaction
for instance by influencing the catalyst size or shape, by providing \( \text{O}_2 \) for the reaction or by formation of an alloy of the metal with the support. Modification of the support can improve the catalyst performance, for example by improving tolerance towards sulfur poisoning of the metal catalyst. The interaction of the catalyst and its support with sulfur species is especially important for applications where sulfur is either the main component in the gas feed, or a relevant minority species.

It is known that materials that are frequently used as catalyst supports are not inert towards sulfur. \( \text{Al}_2\text{O}_3 \), one of the most frequently used catalyst supports is also used as a catalyst for the oxidation of \( \text{H}_2\text{S} \) to elemental \( \text{S} \) (Claus reaction). The surface chemistry of \( \text{Al}_2\text{O}_3 \) in the presence of sulfur was intensely studied, most often using infrared spectroscopy. Activated carbon, another catalyst support, is also used in catalytic oxidation of \( \text{H}_2\text{S} \) or the removal of \( \text{SO}_2 \) from stack gases via adsorption.

Sulfur is a known catalyst poison, for example Ni- or Ru-based methanation catalysts or Fischer-Tropsch catalysts. Since sulfur is contained in natural feedstocks like coal or biomass, regeneration of catalysts for the conversion of such feedstocks is an important research topic.

Infrared spectroscopy probes all species in the gas phase and on the catalyst surface that have a change of molecular dipol moment upon irradiation. Therefore, the spectrum not only contains the sulfur species of interest, but also signatures of other species, such as steam. One direct way to specifically probe the sulfur speciation on catalysts under reaction conditions is X-ray absorption spectroscopy (XAS) at the S K-edge (2474 eV). While ex situ experiments are straightforward to conduct, they suffer from possible interaction of the sample with air, which might change the oxidation state of sulfur significantly, and they offer no time resolution. A recent ex situ XAS study at the sulfur K-edge showed that sulfur poisoning of \( \text{Al}_2\text{O}_3 \) supported Ni reforming catalysts at 900 °C produced mostly sulfides and sulfates, while sulfates were formed after regeneration in \( \text{H}_2\text{O} \) or \( \text{H}_2\text{O} + \text{O}_2 \).

In situ XAS studies are an excellent tool to study sulfur speciation under operating conditions, but few in situ studies have been reported. This is probably due to the limited number of beamlines which allow access to the sulfur K-edge, and therefore the limited available beamtime. In addition, such studies present high requirements from the experimental side. Not only needs the reactor to be tight against high vacuum, but also the windows need to be transparent to the low-energy X-rays, temperature resistant, chemically inert and must not contain elements which
absorb in the desired energy range. In situ studies on SO\textsubscript{x} storage materials, containing Ba on a CuO-Al\textsubscript{2}O\textsubscript{3} support, revealed that SO\textsubscript{2} release under rich conditions is caused by reduction of sulfite species in the presence of Pt. \cite{163} Pt/BaO/Al\textsubscript{2}O\textsubscript{3} materials for NO\textsubscript{x} trapping were studied by sulfur K-edge XAS, providing insights to the mechanism of sulfidation. \cite{164}

In this chapter, the interaction of two commonly used support materials, Al\textsubscript{2}O\textsubscript{3} and C, with H\textsubscript{2}S was studied. To this end, sulfur K-edge XAS was employed to study sulfur speciation of supported Ru catalysts in situ, during poisoning, oxidative regeneration, and subsequent reactivation. This allows proposing a mechanism for sulfur poisoning and regeneration, taking into account the role of the support. Therefore, this chapter is complementary to chapter 5 where the same Ru/Al\textsubscript{2}O\textsubscript{3} catalyst was studied by Ru K-edge XAS. It was found that the Ru/Al\textsubscript{2}O\textsubscript{3} forms sulfide and sulfate species upon poisoning, with the sulfides being on the Ru catalyst and the sulfates being on the Al\textsubscript{2}O\textsubscript{3} support. Upon regeneration, the catalyst activity is restored and the sulfide species are removed from the catalyst. Sulfur species are however stored on the support. Under reducing conditions, sulfur is however transported back to the Ru catalyst, leading to slow deactivation. The C supported Ru catalyst also forms Ru sulfide species and sulfate on the C support. However, the Ru/C catalyst cannot be reactivated by oxidation at 300 °C, which is probably because not all Ru-sulfide species are removed by oxidation.
6.3 Methods and materials

6.3.1 Materials

Ru catalysts supported on different supports, and the blank supports, were investigated in this study. One of the most common catalyst supports is $\gamma$-Al$_2$O$_3$, while activated carbon exhibits remarkable stability under certain conditions, such as gasification in supercritical water. [165,166] Ru/Al$_2$O$_3$ was prepared by wet impregnation of Ru-nitrosyl-nitrate (SigmaAldrich) on $\gamma$-Al$_2$O$_3$ support (Sasol) and showed a size of the Ru particles of 10 - 30 nm (see Figure (5.2)). A Ru/C catalyst was provided by BASF, which has been investigated extensively before, exhibiting a particle size of approximately 1 nm. [166]

6.3.2 XAS measurements

In situ XAS at the sulfur K-edge (2472 eV) was carried out at the PHOENIX beamline X07MB at the Swiss Light Source. The fluorescence signal was acquired with a single element, silicon drift detector (Roentec), that was placed at 90° angle with respect to the X-ray beam. The optical design of the PHOENIX beamline is very similar to the layout of the LUCIA beamline, that is now located at SOLEIL, France. [167] All XAS spectra were normalized to the countrate above the absorption edge, at 2495 eV.

6.3.3 In situ reactor

10-15 mg of the catalyst sample were filled between plugs of quartz wool in a reactor described elsewhere. [168] The reactor was mounted on a XYZ sample stage in a vacuum chamber in a 45° angle with respect to the X-ray beam. The sample was kept in place by Kapton foils (Goodfellow), with a thickness of 13 $\mu$m on the X-ray exposed window and 25 $\mu$m on the opposite window of the reactor.

6.3.4 Gas mixing and analysis

Product gases were dosed with mass flow controllers (Bronkhorst) and analyzed with a quadrupole mass spectrometer (Max 300-LG, Extrel). All stainless steel tubes outside the actual reactor were coated with quartz to minimize sulfur adsorption (Restek).

H$_2$S and SO$_2$ uptake of blank supports

The uptake of H$_2$S and SO$_2$ by the blank supports was tested at 300 °C. The amount of the adsorbed gases was calculated in comparison to a measurement of the empty tube. The supports
were exposed to 1000 ppm H₂S and 8 % O₂ + 80 ppm SO₂, respectively at a total flow of 25 ml min⁻¹.

**In situ experimental procedure**

After the reactor was cleaned and filled with a fresh sample, it was mounted in the vacuum chamber and tested for tightness. Subsequently the vacuum chamber was evacuated to 10⁻⁵ - 10⁻⁴ mbar, and the reactor was heated up to 300 °C under He atmosphere and overpressure of 0.5 - 1 bar (against ambient pressure). If not indicated otherwise, spectra were measured subsequently under the following conditions, with a total flow rate between 20 and 26 ml min⁻¹, and balance inert gas:

1. fresh catalyst under He
2. in 2 % H₂ + 0.2 % CO (10:1)
3. with 96 ppm H₂S added to the H₂ / CO feed
4. in 0.4 % O₂ (at 200 - 400 °C)
5. in 2 % H₂ (+ 0.2 % CO)

As shown in chapter 5, oxidative treatment can, at least partially, reactivate sulfur poisoned Ru catalysts. Due to the properties of the polyimide foil that was used as reactor window, the temperature was limited to ~ 400 °C. In order not to risk oxidation of the C support, the Ru/C was regenerated at a maximum temperature of 300 °C.
6.4 Results

6.4.1 Sulfur uptake of blank supports

To assess the reactivity of the blank supports towards H$_2$S and SO$_2$ adsorption, the supports were exposed to a gas stream of 1000 ppm H$_2$S in inert gas (Ar + He) at a total flow rate of 25 ml min$^{-1}$ at 300 °C. The measured concentration of H$_2$S at the reactor outlet is shown in Figure 6.1(a) for the empty reactor, and the reactor filled with Al$_2$O$_3$ and C. The amount of sulfur adsorbed is calculated here as the time until H$_2$S breakthrough (i.e. detection at the reactor outlet) multiplied with the amount of H$_2$S that was flowing through the reactor until that time. The breakthrough is defined here as the time when H$_2$S signal exceeds 20 ppm. It was found that the blank Al$_2$O$_3$ support absorbs 24 µ-mol H$_2$S / g support and the carbon support absorbs 407 µ-mol H$_2$S / g support.

The product of catalyst regeneration, SO$_2$, can also react with the catalyst support. SO$_2$ breakthrough was defined here as the point in time, when the outlet signal reached 8 ppm SO$_2$. The mass spectrometry signal at m/z 64 (SO$_2$) at the reactor outlet is shown in Figure 6.1(b) for the empty reactor, and the reactor filled with Al$_2$O$_3$ and C. In contrast to H$_2$S uptake, SO$_2$ uptake of both supports was similar, with 160 µ-mol SO$_2$ / g support adsorbed on Al$_2$O$_3$ and 176 µ-mol SO$_2$ / g support adsorbed on the activated carbon.

These results demonstrate already that at 300 °C the two tested blank catalyst supports adsorb relevant amounts of H$_2$S and SO$_2$, which is the product of oxidative regeneration. The C support adsorbs approximately 17 times more H$_2$S than the Al$_2$O$_3$ support, while the amount of SO$_2$ that is adsorbed by both supports is on a similar level.
6.4. RESULTS

6.4.2 Ru/Al₂O₃ and blank Al₂O₃

To study the oxidation state of sulfur during sulfur poisoning and regeneration, XAS spectra were collected in situ. Under sulfur-free H₂ / CO atmosphere, the Ru/Al₂O₃ catalyst is active for methanation. Figure (6.2) shows the mass spectrometry data during sulfur-free methanation, after addition of H₂S, and subsequent oxidative regeneration. After regeneration, sulfur-free feed of H₂ and CO leads again to methanation with high initial activity, which drops slowly over time.

![Figure 6.2: Measured CH₄ and O₂ concentration for the Ru/Al₂O₃ sample during sulfur-free methanation, with H₂S added to the feed and after oxidative regeneration.](image)

Figure (6.3) shows the in situ sulfur K-edge spectra after poisoning, after regeneration and during subsequent, re-activated methanation (the colors of the spectra correspond to the points in Figure (6.2)). Corresponding to the identification of peaks by Hay et al [169] and Almkvist et al [170], we refer in the following to the sulfate (−SO₄²⁻, S⁺VI) peak at 2482 eV, sulfite (−SO₃⁻², S⁺IV) peak at 2478 eV, thiol (−SH, S⁻II) peak at 2473.5 and the sulfide (S⁻II) peak at 2472 eV. When the Ru/Al₂O₃ catalyst is exposed to H₂S containing feed, the fluorescence signal at three energies in the sulfur XAS spectrum (2470.5 eV, 2478 eV and 2481.5 eV) increases over time, indicating formation of sulfide, sulfite and sulfate. Simultaneously, the methanation activity decreases over time until no more CH₄ is produced, which coincides with the XAS spectrum no longer changing over time.

Upon oxidation, the sulfide signal at 2470.5 eV disappears, the sulfite signal at 2478 eV decreases, while the sulfate signal at 2481.5 eV increases. Subsequent exposure of the catalyst to H₂ / He atmosphere leads to a re-appearance of the sulfide peak. The methanation activity is recovered to almost initial level, after which it decreases slowly over time (see Figure (6.2)). The oxidation - reduction cycle was repeated three times, showing reproducibly the disappearing / re-appearing
of the sulfide signal upon oxidation and reduction as shown in Figure (6.3).

A control experiment with blank Al$_2$O$_3$ (see Figure (6.4)) showed a sulfate peak at 2482 eV and a weak signal at 2473 eV upon H$_2$S feed. The signal at 2373 eV is most likely a thiol species. It was shown by Saur et al. with infrared spectroscopy that chemisorption of H$_2$S on Al$_2$O$_3$ leads to Al-SH species. [145] Upon oxidation, the sulfate peak intensity increased significantly relative to the thiol peak intensity. Subsequent exposure to H$_2$ / He further increased the sulfate peak intensity, while the intensity at other energies remained unchanged. No sulfide signal was detected, implying that the sulfide signal found with the Ru/Al$_2$O$_3$ catalyst is indeed due to ruthenium sulfide.

### 6.4.3 Ru/C and blank C

For comparison, similar experiments as with the Ru/Al$_2$O$_3$ catalyst were performed with the Ru/C catalyst. Under sulfur-free atmosphere, the Ru/C catalyst is active for methanation. When H$_2$S is added to the feed, the methanation activity drops to zero over time, while the XAS spectrum (Figure (6.5)) shows a growing peak at 2470.5 eV and no detectable sulfite or sulfate signal. Oxidation at 200 °C leads to a strong decrease in intensity of the peak at 2470.5 eV, while a small peak at 2473.5 eV and a sulfate peak at 2482 eV appears. In accordance with Almkvist et al, we ascribe the peak at 2473.5 eV to a thiol group. [170] Subsequent exposure to H$_2$ / CO at 300 °C leads to reappearance of the sulfide peak at 2470.5 eV and a significant decrease of the sulfate peak intensity, while the signal at 2473.5 eV remains. However, this
6.4. RESULTS

Figure 6.4: Sulfur K-edge XAS spectrum of the blank Al$_2$O$_3$ support after exposure to H$_2$ / H$_2$S (red triangles), O$_2$ (green squares) and subsequent H$_2$ exposure (blue diamonds). The inset shows a magnification of the energy range from 2465 eV to 2480 eV.

The blank carbon support shows two distinct peaks upon H$_2$ / CO / H$_2$S feed, at 2481.5 eV and 2473.5 eV, with a shoulder at 2471.5 eV (see Figure 6.6). Upon oxidation, the sulfate peak at 2481.5 eV increases significantly, while the intensity of thiol peak 2473.5 eV and the shoulder at 2471.5 eV decrease. Under subsequent exposure to H$_2$ / CO, the spectrum does not change.
significantly.

Figure 6.6: Sulfur K-edge XAS spectrum of the blank C support after exposure to $\text{H}_2 / \text{CO} / \text{H}_2\text{S}$ (red triangles), oxidation in $\text{O}_2$ at 200 °C (green squares) and subsequent $\text{H}_2$ exposure at 300 °C (blue diamonds).
6.5 Discussion

6.5.1 Sulfur transport over Ru/Al₂O₃

The results of the in situ experiments on Ru/Al₂O₃ and blank Al₂O₃ imply that a gas feed containing H₂S to the Ru/Al₂O₃ catalyst leads to formation of sulfides and sulfates, which are most likely in the form of RuSₓ and Al₂(SO₄)₃ on the surface of the Ru and Al₂O₃, respectively. Formation of RuSₓ was already observed by Ru K-edge XAS in chapter 5. Oxidation removes the sulfides and also increases the fraction of sulfates. The increase of the sulfate signal in Figure 6.3 upon subsequent reduction is most likely due to sulfur that is released from the beginning of the catalyst bed (upstream of the point that is probed with the X-rays). This sulfur then reacts with the alumina support to form more Al₂(SO₄)₃.

The fact that methanation activity is restored makes it plausible that most sulfur is removed from the Ru, such that RuS₂ reacts with O₂, forming RuO₂ and SO₂ (see chapter 5). Transition from Ru to RuO₂ upon oxidation is detected in earlier Ru K-edge experiments (see chapter 5). Part of the SO₂ that is formed in the process reacts with Al₂O₃, creating more Al₂(SO₄)₃. Subsequent exposure to H₂ leads to reduction of RuO₂ to Ru, while some Al₂(SO₄)₃ is reduced to Al₂O₃ and H₂S, which reacts again with Ru, leading to the observed formation of sulfides and the slow drop in activity over time. The sulfide species are observed immediately upon reduction, while the catalyst is still active for methanation. This can be interpreted in two ways: either the catalyst activity comes from those catalyst particles that are not probed by the X-rays (i.e. up- or downstream in the reactor), or only a fraction of active Ru sites is poisoned first, while there are still non-poisoned active sites, which only become deactivated over a longer time (several minutes in this experiment).

Based on the presented results in this chapter and in chapter 5 the following mechanism is proposed:

Poisoning

\[ Ru/Al₂O₃ + H₂S \rightarrow RuSₓ/Al₂(SO₄)₃ + H₂ \] (6.1)

Oxidation

\[ RuSₓ/Al₂(SO₄)₃ + O₂ \rightarrow RuO₂/(Al₂O₃ + Al₂(SO₄)₃) + SO₂ \] (6.2)

Reactivation

\[ RuO₂/Al₂(SO₄)₃ + H₂ \rightarrow Ru/(Al₂O₃ + Al₂(SO₄)₃) + H₂S + H₂O \] (6.3)

In the oxidation (reaction 6.2), only a fraction of the sulfate species in aluminum sulfate are converted to SO₂. Under the following reducing conditions for reactivation another fraction is reduced with H₂ to H₂S. Repeating the cycle of oxidation and reactivation in sulfur-free atmosphere several times removes more and more sulfur and therefore leads to less deactivation.
over time on stream (see Figure 5.7b). However, activity could not be fully recovered over the 15 tested cycles.

6.5.2 Sulfur transport over Ru/C

Activated carbon is used at mild temperatures to adsorb H$_2$S or SO$_2$ and exposed to higher temperatures (~450 °C) to regenerate the carbon, i.e. remove the sulfur, in inert gas. However, only few studies on sulfur poisoning of carbon supported catalysts exist (see e.g. [165]).

Similar to the Ru/Al$_2$O$_3$ catalyst, the low energy peak at 2470.5 eV in the Ru/C spectrum (Figure 6.5) can be attributed to RuS$_x$, because it coincides with the loss of methanation activity, and is largely absent in the blank carbon support. The peak at 2473 eV is likely to be due to a thiol group of sulfur that chemisorbed on an OH group on the carbon’s surface [171], while the peak at 2482 eV is due to a sulfate group on the carbon’s surface. This implies that, on the fresh Ru/C catalyst, sulfur preferentially adsorbs to the Ru as sulfide, and is only transported to the carbon support upon oxidation as sulfate and some thiol. However, even after oxidation, not all sulfide species are removed, in contrast to the Ru/Al$_2$O$_3$ catalyst (see Figure 6.3). When the Ru/C catalyst is subsequently exposed to sulfur-free methanation conditions, a major part of the sulfate is quickly reduced to sulfide, poisoning the Ru catalyst again, which is supported by the increased peak intensity at low energy (2470.5 eV). In the spectra of the blank C support, the decrease in intensity of the sulfate peak with simultaneous increase in intensity of the sulfide peak is absent, indicating that Ru plays an important role for the observed phenomena.

In addition, it is also possible that not all sulfur was removed from the Ru surface in the first place, leaving the most active sites poisoned. This is supported by the small remaining peak in the XAS spectrum at 2470.5 eV under O$_2$ atmosphere (Figure 6.5). In conclusion, the following mechanism is proposed:

Poisoning

$$\text{Ru/C} + \text{H}_2\text{S} \rightarrow \text{RuS}_x/C + \text{H}_2 \quad (6.4)$$

Regeneration

$$\text{RuS}_x/C + \text{O}_2 \rightarrow \text{RuO}_2/C + \text{SO}_4^{2-}(\text{ads})/\text{C} \quad (6.5)$$

Reactivation with subsequent poisoning

$$\text{RuO}_2/C + \text{SO}_4 - 2(\text{ads})/\text{C} + \text{H}_2 \rightarrow \text{Ru/C} + \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{RuS}_x/C \quad (6.6)$$

Both catalysts that were tested in this study (Ru/Al$_2$O$_3$ and Ru/C) are prone to sulfur poisoning. On the Ru/Al$_2$O$_3$ catalyst, sulfur adsorbs to both, the Ru metal (as sulfide) and the support (as sulfate), and upon regeneration, the sulfide disappears while the amount of sulfate increases.
Subsequent re-activation in $H_2 + CO$ leads to sulfur transport from the support back to the metal, slowly reducing activity. On the other hand, sulfur preferentially binds to Ru in the Ru/C catalyst during initial exposure to $H_2 + CO + H_2S$ (see Figure 6.5). Only after oxidation a sulfate species and a thiol species forms, most likely on the carbon support. Subsequent re-activation transports the sulfur quickly back from the support to the Ru metal, therefore effectively hindering regeneration. These observations are similar to what Yung et al found in ex situ XAS studies on $Al_2O_3$ supported Ni catalysts that were poisoned and regenerated at 900 °C. However, their Ni-based catalyst seems not suited for methanation, since Ni forms NiSO$_4$ upon regeneration in O$_2$ which is very stable at temperatures below 850 °C and is therefore irreversibly poisoned, unless the O$_2$ partial pressure during regeneration is very low, which leads to long regeneration times.

6.5.3 Implications for sulfur storage on support materials

This study shows by direct means that the catalyst support stores sulfur, and that this storage function impacts the catalyst regenerability in a negative fashion. In order to optimize regenerability, the sulfur storage capacity should be either minimized, or the removal of sulfur from the support during regeneration should be facilitated.

Future work could therefore focus on the modification of the support, for instance by addition of dopants, in order to minimize sulfur uptake, or facilitate decomposition of sulfates under oxidizing conditions at low temperatures. Such dopants could be Li or K, which were shown to facilitate decomposition of aluminum sulfate at lower temperatures, compared to pure $Al_2O_3$, thereby improving regeneration efficiency. Doping of Ag / $Al_2O_3$ catalysts with SiO$_2$ or TiO$_2$ led to increased tolerance towards SO$_2$ poisoning. Comparison of $Al_2O_3$ with Na-doped $Al_2O_3$ showed lower reactivity of Na-doped $Al_2O_3$ towards H$_2$S, compared to $Al_2O_3$. On the other hand, doping with Na increased the amount of adsorbed SO$_2$ on $Al_2O_3$ supports. These examples show that modification of the supports can change the reactivity of the supports towards sulfur, which can be beneficial for improving the regeneration efficiency of sulfur-poisoned methanation catalysts.
6.6 Conclusion

In this chapter, sulfur poisoning and regeneration of Ru catalysts on two different supports (Al$_2$O$_3$ and activated carbon), and the blank supports, was studied with in situ X-ray absorption spectroscopy at the sulfur K-edge. Under methanation conditions (exposure of the catalyst to H$_2$ and CO at 300 °C), it was found that Ru sulfide species are formed upon exposure to H$_2$S on both catalysts. After oxidation, the Ru sulfide disappears, and sulfur is detected only as sulfate. Subsequent reduction leads to re-formation of sulfide species, which coincides with slow deactivation of the Ru/Al$_2$O$_3$ catalyst. The Ru/C catalyst however was not regenerated by oxidative treatment at 300 °C. For the Al$_2$O$_3$ support catalyst, a mechanism is proposed, which includes formation of Al$_2$(SO$_4$)$_3$ that is slowly dissolved under reducing conditions, leading to the observed deactivation under sulfur-free conditions after an initial poisoning - regeneration cycle. For the Ru/C catalyst, the sulfate on the carbon support is quickly transported back to the Ru under reducing conditions, making regeneration not possible under the tested reaction conditions.

This chapter highlights the role of the catalyst for the ability and efficiency of catalyst regeneration after sulfur poisoning. Development of protocols for effective sulfur removal from the support, or modification of support materials for minimized sulfur uptake, is required to optimize regenerability.
Chapter 7

Conclusions

This thesis provides mechanistic insights into possible concepts for high-temperature sulfur cleaning of biomass-derived producer gas (chapters 3 - 6) as well as methodological advancements (chapter 2), which are needed to reveal such mechanisms. The studied concepts have the potential to reduce costs of biomass conversion, and therefore to contribute to establishing competitive biomass conversion technologies.

Chapter 2 contains an approach for quantification of time-resolved EXAFS spectra that were obtained while applying the modulated excitation concept. By examination of simulated and experimental data, it was shown that this approach allows detecting and quantifying small differences in a sample’s structure. In chapter 5, this quantitative approach was extended to more complex cases, bringing it closer to realistic experiments. Modulated excitation spectroscopy pushes the sensitivity of EXAFS beyond the limits that are typical for standard EXAFS measurements, ultimately allowing better understanding of the processes taking place on the sample. While being especially useful for studying catalysts, this approach can potentially be beneficial for a wide range of experiments, from functional materials over electrochemical systems to magnetism or photochemistry.

In chapter 3 an approach for bulk removal of H₂S by Mn-based sorbents was investigated by means of mass spectrometry and XAS. From these measurements, a mechanism for sulfur transport over Mn-based materials could be proposed, highlighting an unexpected side-reaction that inhibits full sulfur-removal. Notwithstanding, using Mn-containing materials in the gasifier instead of sand is a feasible option for bulk gas cleaning. Ultimately, its applicability as desulfurization material will depend on the costs of the material, and the benefits for downstream processes.

While manganese is not reactive towards thiophene, molybdenum is widely used for desulfurization of hydrocarbon feedstocks. In chapter 4 an approach for removing H₂S and C₄H₄S over Mo-based catalysts was studied. Since the requirements for cleaning of sulfur-containing producer gas from biomass are different from the standard case of hydrodesulfurization in industry in
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terms of steam content, temperature and H2 pressure, a dedicated investigation was required. The mechanism for removal of H2S was found to be sulfidation of MoO3 to MoS2, while C4H8S is removed by conversion to hydrocarbons and adsorbed sulfur on the MoO2 surface. It was shown that steam negatively influences the sulfur removal, presumably by blocking active sites for adsorption of C4H8S. However, Mo-based catalysts are promising candidates for stable sulfur removal from biomass-derived producer gas under cyclic operation at high temperatures.

An integrated approach for simultaneous removal of sulfur, containing also organic sulfur compounds such as thiophene, and methanation over supported Ru catalysts was studied in chapter 5. It was found that the catalyst is successfully regenerated with O2 over multiple cycles while sulfur is removed from the gas stream. While the catalyst is regenerated after oxidation, activity was found to decrease over time-on-stream, even in the absence of sulfur. A mechanism for cyclic catalyst poisoning and regeneration was proposed. This mechanism explains the observed deactivation in absence of sulfur in the gas stream with sulfur transport from the support to the Ru catalyst. Moreover, no permanent formation of Ru-sulfides was observed with XAS. Applying the modulated excitation approach to the time-resolved EXAFS data showed that small amounts of Ru-sulfides are formed and dissolved over the sequence of poisoning and regeneration. Even though Ru is an expensive material, the prospect of such an integrated process, allowing to omit the cold gas cleaning and at least minimizing a final methanation reactor, can outweigh the costs.

For a better understanding of the influence of the support on sulfur poisoning and regeneration of poisoned catalysts, the state of sulfur was studied in chapter 6. While being experimentally challenging, in situ studies at low X-ray energies allow sensitive speciation of sulfur, and thereby are complementary to the studies at the Ru K-edge in chapter 5. It was clearly shown that oxidative treatment of sulfur poisoned catalysts does remove the sulfide species which are causing the poisoning. Sulfur remains as sulfate, presumably on the Al2O3 support, which is responsible for subsequent re-poisoning. This motivates specific development of support materials with low affinity to sulfur, which should improve the integrated process for sulfur removal and methanation, presented in chapter 5.
Chapter 8

Outlook and recommendations for future work

To further develop the methods used in this thesis, and to improve the process for generation of synthetic natural gas from wood, the following recommendations for further research can be given on the basis of this thesis:

8.1 Modulated excitation spectroscopy

For further development of the modulated excitation spectroscopy, mainly two paths are proposed:

First, kinetics of the reaction can be extracted by analyzing higher-order terms of the demodulation formula (equation 2.1). The good time resolution that is offered by QuickXAS (up to 40 Hz) can be used in combination with a sufficiently fast experimental setup (fast valve switching, little dead volumes, fast gas analysis) to compare the real kinetics at different excitation frequencies with those which are predicted by analysis of the demodulated spectra.

Second, more complex excitation of a system, for example by multiple steps, can be investigated in greater detail. While the analysis scheme that is proposed in section 5.3.5 is very generic, systematic experiments are needed to determine what the limits of detection are.

8.2 Desulfurization

While the mechanism that was found for high-temperature desulfurization over Mn-based materials seems to prevent complete sulfur removal due to the formation of SO$_2$, there are further questions that are worth investigating. Utilization of Mn-based materials in gasifiers could be
interesting for bulk removal of sulfur. Investigating this application in greater details could be done either in real gasifiers, or under simulated conditions.

Next steps for the investigation of high temperature removal of organic and inorganic sulfur species over Mo-based catalysts should go along two directions, which are ultimately coupled to each other: first, the performance of the catalyst should be investigated under realistic, or close-to-realistic conditions, where the producer gas not only contains one sulfur species, but a variety of sulfur species, tars, olefins and other compounds that are typically found in producer gas after filtering. Such investigations will give a better picture of the applicability or limits of the gas cleaning capabilities of Mo-based catalysts. Second, systematic materials development should be performed, starting with typical HDS catalyst formulations, such as Co-Mo or Ni-Mo catalysts. However, the conditions of high-temperature gas cleaning of producer gas, that are rather different from HDS conditions, should be kept in mind. This relates especially to the presence of steam, and the periodic oxidation that is performed in the chosen approach. For instance, oxidation of sulfided Ni-Mo catalysts can lead to formation of Ni-sulfates.

8.3 Ru based high-temperature gas cleaning with integrated methanation

To further develop the proposed process of integrated methanation and sulfur removal over Ru-based catalysts, the process needs to be defined more precisely, and improved materials need to be developed. Before that, the boundary conditions need to be defined. For instance, two extreme scenarios could be defined, one for the best case, where the producer gas is already cleaned from significant amounts of sulfur, olefins and tars, and one worst-case scenario, where the composition of the gas is very close to that of the gasifier exit. The best-case scenario could be based on the performance of other gas cleaning methods, such as reactive bed materials in the gasifier (e.g. Mn-based materials), reactive filters or tar reforming, which remove already major portions of the catalyst poisons and/or reform parts of the tars and olefins.

Next, a Ru based catalyst would be exposed to those two conditions (best case and worst case) at different temperatures between 300 and 800 °C. This allows evaluation of a favorable regime for the different constraints and goals (methane synthesis, sulfur removal, tar removal). For those temperatures that are promising, the regeneration conditions (time and temperature) can be varied.

Once the conditions under which this process yield good results - in terms of methane output and gas cleaning - are constrained to a rather narrow parameter field, dedicated materials development can start. This would include variation and modification of support materials, which were shown to influence the sulfur transport or the addition of secondary metals, which could preferentially adsorb sulfur (e.g. Zn, Mn, Mo, Cu or others).
Finally, if process conditions and a material are found that satisfy the goals (complete CO conversion and / or complete gas cleaning), kinetic tests can be performed, for the process to be scaled up.

8.4 Understanding sulfur adsorption on supports

To develop more sulfur-inert supports, a better understanding of the mechanisms of sulfur adsorption and desorption on support materials is required. Besides sulfur K-edge XAS (see chapter [9]), infrared spectroscopy is an excellent tool to study adsorbed species under realistic conditions. Together with specific modification of the support materials, e.g. by promoting with other elements, or chemical modification of the surface, spectroscopic techniques can provide mechanistic insight into sulfur adsorption and removal, and ultimately contribute to development of supports that allow better regeneration.
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