Catalytic conversion of syngas to higher alcohols over MoS$_2$-based catalysts

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I am among those who think that science has great beauty. A scientist in his laboratory is not only a technician: he is also a child placed before natural phenomena which impress him like a fairy tale.

Marie Curie
Abstract

The present thesis concerns catalytic conversion of syngas \((H_2 + CO)\) into a blend of methanol and higher alcohols, an attractive way of producing fuels and chemicals. This route has the potential to reduce the oil dependence in the transport sector and, with the use of biomass for the syngas generation, produce CO\(_2\)-neutral fuels.

Alkali promoted MoS\(_2\)-based catalysts show a high selectivity to higher alcohols, while at the same time being coke resistant, sulfur tolerant and displaying high water-gas shift activity. This makes this type of catalyst especially suitable for being used with syngas derived from biomass or coal which typically has a low H\(_2\)/CO-ratio.

This thesis discusses various important aspects of higher alcohol synthesis using MoS\(_2\)-based catalysts and is a summary of four scientific papers. The first part of the thesis gives an introduction to how syngas can be produced and converted into different fuels and chemicals. It is followed by an overview of higher alcohol synthesis and a description of MoS\(_2\)-based catalysts. The topic alcohol for use in internal combustion engines ends the first part of the thesis.

In the second part, the experimental part, the preparation of the MoS\(_2\)-based catalysts and the characterization of them are handled. After describing the high-pressure alcohol reactor setup, the development of an on-line gas chromatographic system for higher alcohol synthesis with MoS\(_2\) catalysts is covered (Paper I). This method makes activity and selectivity studies of higher alcohol synthesis catalysts more accurate and detailed but also faster and easier. Virtually all products are very well separated and the established carbon material balance over the reactor closed well under all tested conditions. The method of trace level sulfur analysis is additionally described.

Then the effect of operating conditions, space velocity and temperature on product distribution is highlighted (Paper II). It is
shown that product selectivity is closely correlated with the CO conversion level and why it is difficult to combine both a high single pass conversion and high alcohol selectivity over this catalyst type. Correlations between formed products and formation pathways are additionally described and discussed. The CO₂ pressure in the reactor increases as the CO conversion increases, however, CO₂ influence on formation rates and product distribution is to a great extent unclear. By using a CO₂-containing syngas feed the effect of CO₂ was studied (Paper III).

An often emphasized asset of MoS₂-based catalysts is their sulfur tolerance. However, the use of sulfur-containing feed and/or catalyst potentially can lead to incorporation of unwanted organic sulfur compounds in the product. The last topic in this thesis covers the sulfur compounds produced and how their quantity is changed when the feed syngas contains H₂S (Paper IV). The effect on catalyst activity and selectivity in the presence of H₂S in the feed is also covered.

**Keywords:** catalytic conversion; higher alcohols; mixed alcohols; MoS₂; syngas
Sammanfattning

Titel: Katalytisk omvandling av syntesgas till högre alkoholer över MoS$_2$-baserade katalysatorer.

Denna avhandling behandlar katalytisk omvandling av syntesgas (H$_2$ + CO) till en blandning av metanol och högre alkoholer, ett attraktivt sätt att producera bränslen och kemikalier. Denna produktionsväg har potential att minska oljeberoendet i transportsektorn och, om biomassa används för produktionen av syntesgas, kan dessutom CO$_2$-neutrala bränslen framställas.

Alkaliberikade MoS$_2$-baserade katalysatorer uppvisar en hög selektivitet till högre alkoholer, medan de samtidigt är koksresistenta, svaveltoleranta och påvisar hög vattengasskift-aktivitet. Detta gör denna typ av katalysator speciellt lämpad för användning med syntesgas producerad från biomassa eller kol, som typiskt har ett lågt H$_2$/CO-förhållande.


I den andra delen, den experimentella delen, behandlas framställningen av MoS$_2$-baserade katalysatorer och deras karakterisering. Efter att högtrycksreaktorn för alkoholsyntes beskrivits, följer en beskrivning av utvecklingen av ett ”on-line” gaskromatografiskt system för syntes till längre alkoholer med MoS$_2$-baserade katalysatorer (Publikation I). Den här metoden gör aktivitets- och selektivitetsstudier av katalysatorer för högre
alkoholer från syntegas mer exakta och detaljerade men också snabbare och enklare. Så gott som alla produkter separeras mycket väl med denna metod och den upprättade kolmaterialbalansen över reaktorn stänger mycket väl under alla testade förhållanden. Analysmetoden för mätning av svavel i mycket låga halten beskrivs också.


Publications referred to in this thesis

The work presented in this thesis is based on the following publications. The papers are appended at the end of the thesis, and are referred to in the text using Roman numerals.

I. R. Andersson, M. Boutonnet, S. Järås
   *On-line gas chromatographic analysis of higher alcohol synthesis products from syngas*

II. R. Andersson, M. Boutonnet, S. Järås
    *Correlation patterns and effect of syngas conversion level for product selectivity to alcohols and hydrocarbons over molybdenum sulfide based catalysts*

III. R. Andersson, M. Boutonnet, S. Järås
    *Effect of CO$_2$ in the synthesis of mixed alcohols from syngas over a K/Ni/MoS$_2$ catalyst*

IV. R. Andersson, M. Boutonnet, S. Järås
    *Higher alcohols from syngas using a K/Ni/MoS$_2$ catalyst: Trace sulfur in the product and effect of H$_2$S containing feed*

**Contributions to the publications:**
I was the main responsible for planning, performing and evaluating the experimental work included in papers I-IV. I was also the main writer of papers I-IV.
Conference contributions

R. Andersson, Y. Xiang, M. Boutonnet, S. Järås, N. Kruse
*Chemical Transient Kinetics Applied to CO hydrogenation over Molybdenum sulfide based catalysts*

R. Andersson, M. Boutonnet, S. Järås
*Effect of temperature and space velocity in Ethanol and Higher Alcohol Synthesis from syngas over Molybdenum-based catalysts*
Poster presented at the Nordic symposium on catalysis, Marienlyst, Danmark, 2010.

S. Lögdberg, M. Lualdi, R. Andersson, F. Regali, M. Boutonnet, S. Järås
*Biofuels from gasified biomass*
Poster presented at COST Action CM0903 workshop, Córdoba, Spain, 2010.

R. Andersson, M. Boutonnet, S. Järås
*Ethanol and higher alcohol synthesis from syngas over molybdenum-based catalysts from microemulsion*
Poster presented at EuropaCat IX: Catalysis for a Sustainable world, Salamanca, Spain, 2009.

M. Lualdi, S. Lödgberg, R. Andersson, S. Järås, D. Chen
*Nickel-Iron-Aluminum-hydrotalcite derived catalysts for the methanation reaction*
Poster presented at EuropaCat IX: Catalysis for a Sustainable world, Salamanca, Spain, 2009.
R. Andersson, M. Boutonnet, S. Järås

*Ethanol and Higher Alcohol Synthesis from syngas over Molybdenum-based catalysts*

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Chapter 1

Introduction

1.1 Setting the scene

One of the most important challenges that mankind has to face in the upcoming years, is to secure energy supply for an ever energy-thirstier world, while at the same time minimizing the environmental impact and saving the planet [1]. Until 2050 the world population is estimated to grow by more than 33% to 9.6 billion [2]. The population growth together with greater prosperity and incomes in emerging economies drives this increased energy demand. Using energy more efficiently probably is the smartest and least costly ways to extend our world’s energy supplies. However, even with the expected improvements in energy usage a 37% increase in energy use is projected by the year 2040 and a 20% increase in CO₂ emissions [3]. During the same time period the number of cars and trucks on the world’s roads is expected to more than double and the demand for oil for transport to grow by 25% [3].

An interesting alternative for producing liquid fuels and/or chemicals is via the so called synthesis gas route. Syngas can be produced from many different carbon-containing materials, such as coal and natural gas. Biomass is preferably the raw material of choice, since greenhouse gas-neutral fuels can be produced. The syngas can, depending on catalyst and operation conditions used, be converted to either methanol through so-called i.e. methanol synthesis, long hydrocarbons through so-called Fischer-Tropsch synthesis or alcohols longer than methanol through so-called higher alcohol synthesis (HAS). After product upgrading premium liquid fuels are achieved.
1.2 Scope of the thesis

The present thesis concerns the catalytic conversion of syngas (H₂/CO) into a mixture of methanol and higher alcohols. Producing higher alcohols in this way is better known as higher alcohol synthesis (HAS) or mixed alcohol synthesis (MAS) and is an attractive future way for producing fuels and chemicals. Focus in this work is on the use of H₂-poor syngas (with low H₂/CO ratio) which typically is achieved from biomass and coal, while syngas derived from natural gas gives a syngas much richer in H₂. Alkali-promoted MoS₂-based catalysts display a high selectivity to higher alcohols, while at same time being coke resistant, sulfur tolerant and displaying high water-gas shift activity. This makes this type of catalyst especially suitable for being used with syngas derived from biomass or coal.

The present thesis discusses various important aspects related to the field of HAS with alkali-promoted MoS₂ catalysts, based on the main findings from the four appended papers.

- In the first paper (Paper I), the development of a rapid and accurate on-line gas chromatographic system for HAS with MoS₂ catalysts is presented. This makes studies of HAS catalysts more detailed and accurate but also faster and easier.
- In the second paper (Paper II), the effect of operating conditions, space velocity and temperature on product distribution is highlighted. Correlations between formed products, and formation pathways are additionally discussed.
- In the third paper (Paper III), the effect of CO₂-containing feed under constant syngas partial pressures was mainly studied.
• In the fourth paper (Paper IV), possible incorporation of trace sulfur into the alcohol product and the effect on product distribution with and without $\text{H}_2\text{S}$ in the syngas feed is discussed.

The work included in this thesis was conducted at the Department of Chemical Engineering and Technology at the Royal Institute of Technology (KTH), Stockholm, Sweden.
Chapter 2

Syngas and synthetic fuels

![Diagram of syngas generation and conversion routes to fuel and chemicals. Adapted from [4]](image)

Liquid fuels and chemicals can be produced by the so called synthesis gas (syngas) route (see Fig. 2.1). The syngas (H₂/CO) in turn can be created from any suitable carbon source, but the most common raw materials are coal or natural gas. If the carbon source is biomass (e.g. wood or organic wastes) also greenhouse gas-neutral fuels and chemicals can be produced. In countries with available coal, natural gas or biomass sources, the process therefore has the possibility to reduce foreign oil dependence, increase energy security and create employment. A brief overview of this conversion process from feedstock to products via the syngas route will follow in this chapter. The major steps in this process can be seen in Fig. 2.2.
Fig. 2.2. Simplified drawing for production of fuels and chemicals through the synthesis route.

### 2.1 Syngas generation and cleaning

In the production of synthetic fuels and chemicals, the syngas generation, cleaning and conditioning part stands for most of the investment cost and largest part of the energy use in the plant. About 60-70% of the investment cost in a natural gas-based methanol plant is normal [5]. The design of the syngas preparation part is therefore critical for the economics of the whole plant. However, the design of the synthesis gas preparation section will mainly depend on the available feedstock together with the downstream use of the syngas. Good integration of all processes and energy usage is essential for plant efficiency and economy [6]. Obviously, the feedstock availability and price also is vital for plant design, plant size and economy.
2.1.1 Syngas from coal and biomass

The technology for producing syngas is generally separated into two categories, gasification and reforming. Gasification is the term used to describe conversion of solid or heavy liquid feedstock to syngas e.g. coal or biomass, while reforming is used for conversion of gaseous or light liquid feedstock to syngas e.g. natural gas. In gasification the carbon source is combined with steam and/or oxygen to yield a gas containing mainly hydrogen, carbon monoxide, carbon dioxide and methane. The proportions of these component gases depend on a number of parameters such as used feedstock (moisture and composition), gasification medium (steam, oxygen and/or air) and reaction conditions (temperature, pressure) together with gasifier and gasification reaction technology used [7]. There are three main gasifier types (Fig. 2.3): fixed bed (bubbling or circulating), fluidized bed (downdraft and updraft) and entrained flow gasifiers, all with their own advantages and disadvantages [8].

Fig. 2.3. The three most common types of gasifiers. Reproduced with permission from [9].

Once the feedstock has been converted to gaseous state, undesirable substances as such as sulfur (COS, H₂S), nitrogen
(NH₃, HCN) and halogen compounds (HCl) as well as volatile metals (K, Na), particulates (soot, dust, char, ash) and tars (polyaromatics) are removed [10]. The gasification process and the composition of the feedstock determines this contamination level [8].

Syngas generated through coal or biomass gasification typically has a H₂/CO ratio in the range 0.45-1.5 [11, 12]. This means that syngas generated from these resources are much poorer in H₂ and richer in CO than syngas produced from natural gas.

### 2.1.2 Syngas from natural gas

The predominant commercial technology for syngas generation is steam methane reforming (SMR) from natural gas, in which methane and steam catalytically and endothermically are converted to hydrogen and carbon monoxide. An alternative technology is partial oxidation (POX) in which methane and oxygen exothermically is converted to syngas. The two technologies inherently produce syngas with greatly different H₂/CO ratio being about 3-5 in SMR (can be lowered with CO₂ addition) and about 1.6-1.9 in POX [13, 14]. Partial oxidation can

![Diagram of reactors for syngas production from natural gas. Adapted from [4].](image)
be performed both catalytically and non-catalytically. Autothermal reforming (ATR) is a third alternative, which can be seen as a hybrid between the two previous in a single reactor. In the combustion zone, parts of the feed are combusted with oxygen, while in the reforming zone the remaining feed and the produced CO\textsubscript{2} and H\textsubscript{2}O are reformed catalytically to syngas. The required energy for the endothermic reforming reactions is provided by the exothermic oxidation reactions from the combustion zone.

### 2.2 Syngas to products

The search for efficient catalytic processes for fuels and chemicals production from syngas has been going on for more than a century. Early research and development was to a great part performed in Germany in the 1910’s-1940’s and the quest for efficient methanol, higher alcohols and hydrocarbon catalyst share a common history [15, 16].

#### 2.2.1 Methanol, dimethyl ether and methanol-to-gasoline

The first commercial catalyst for converting syngas (H\textsubscript{2}/CO) to methanol was demonstrated by BASF in 1923 [17, 18].

\[
\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \quad \Delta H^\circ_{298K} = -90.5 \text{ kJ/mol} \quad (2.1)
\]

The catalyst contained ZnO-Cr\textsubscript{2}O\textsubscript{3} and was only active at high temperatures (350-400 °C) and therefore very high pressures (240-350 bar) were needed to reach acceptable conversion levels (conversion is thermodynamically limited) [16]. This catalyst formulation was used until the end of the 1960’s due to its resistance towards sulfur, chlorine and group VIII carbonyls even though more active catalysts were known [19]. The easily poisoned
but better Cu-based catalyst thereafter took over since new efficient chemical and physical wash gas cleaning procedures had been developed [20].

At present methanol is in general produced from methane (natural gas) steam reforming, followed by methanol synthesis using a Cu/ZnO/Al₂O₃ catalyst. This modern low pressure (50-100 bar) and temperature (240-260 °C) process (first used in 1966 by ICI) has a selectivity above 99.5%, which is remarkable given the great number of possible by-products, with methanol being one of the least thermodynamically favorable products [16, 19]. Methanol is one of the world’s most heavily traded chemical commodities and every day more than 180,000 tons of methanol is produced in more than 100 plants worldwide [21].

Formed methanol can be dehydrated by a suitable catalyst (e.g. γ-Al₂O₃) to form dimethyl ether (DME) (eq. 2.2) which in addition to being a well-used chemical, can be used as a clean-burning gaseous fuel for use in diesel engines (cetane number 55) [22].

\[
2 \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (2.2)
\]

In the so called methanol-to-gasoline (MTG) process, methanol can be converted to gasoline. In this process methanol is partly dehydrated to produce an equilibrium mixture of methanol, DME and water, followed by conversion to light olefins (C₂-C₄) and in a final reaction step to higher olefins, n/iso-paraffins, aromatics and naphthenes assisted by a zeolite catalyst (ZSM-5) [23].

\[
\text{MeOH} \rightarrow \text{MeOH} + \text{DME} + \text{H}_2\text{O} \rightarrow \text{synthetic gasoline} \quad (2.3)
\]

A fully commercial plant, producing 14,500 bbl/day was operated in New Zealand, 1985-1998. The only presently running MTG plant
came on stream in 2009 in China; it has a capacity of 2,500 bbl/day [24].

2.2.2 Fischer-Tropsch

Fischer-Tropsch (FT) synthesis is a series of reactions converting syngas (H$_2$/CO) into a large spectrum of mainly linear hydrocarbons (eq. 2.4). The name pays tribute to the Germans Franz Fischer and Hans Tropsch who invented the method in the 1920’s [25, 26]. Presently, a handful of industrial Fischer-Tropsch plants are in operation worldwide, operating with syngas derived from natural gas or coal [27].

$$\text{CO} + 2\text{H}_2 \rightarrow \text{-CH}_2^- + \text{H}_2\text{O} \quad \Delta H^\circ_{298K} = -165 \text{ kJ/mol} \quad (2.4)$$

The reaction is industrially performed with iron or cobalt-based catalysts typically at a pressure around 20-40 bar [16]. The product distribution is mainly determined by the operation temperature and the choice of catalyst [6, 28]. Two operation modes exist: High-temperature FT (HTFT) and low-temperature FT (LTFT), which are performed at 300-350 °C and 200-240 °C, respectively. In HTFT, Fe-based catalysts are used and the main products are linear low molecular mass olefins, gasoline and oxygenates [28]. In LTFT, Fe or Co-based catalysts are used for the production of high-molecular linear waxes [28]. A significant difference between Fe and Co catalysts is that the iron catalyst has high water-gas shift activity while the water-gas shift activity for cobalt catalyst is very poor [29, 30]. This means that the H$_2$/CO-usage ratio is much lower with the iron catalyst, due to the simultaneously occurring water-gas shift (WGS) reaction. To achieve a premium fuel, the raw FT product is upgraded to diesel or gasoline using processes such as hydrocracking, isomerization, catalytic reforming and alkylation [6].
2.2.3 Higher alcohols

Higher alcohol synthesis will be covered in a separate chapter, since it is the main concern of this thesis are about.
Chapter 3

**Higher alcohol synthesis**

In the following, a short review of the field of higher alcohols synthesis (HAS) and the most central concepts are presented. The chapter starts with a general introduction to the field of higher alcohol synthesis and the reactions involved. It is followed by a presentation of the most important catalyst classes and processes developed for higher alcohol synthesis, and how the alcohol distributions for these processes look. The development of higher alcohol synthesis from the start in the early 20th century until present is briefly covered as well as the thermodynamic limits imposed in HAS.

### 3.1 Introduction

Higher alcohol synthesis (HAS) is a series of exothermic reactions, where CO and H₂ (syngas) are converted into short alcohols over a catalyst (Eqs. 3.1-3.5). A substantial part of the alcohols should also be longer than methanol, thus the name.

\[
\begin{align*}
\text{CO} + 2 \text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} & \text{Methanol} & (3.1) \\
2 \text{CO} + 4 \text{H}_2 & \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} & \text{Ethanol} & (3.2) \\
3 \text{CO} + 6 \text{H}_2 & \rightleftharpoons \text{C}_3\text{H}_7\text{OH} + 2 \text{H}_2\text{O} & \text{Propanol} & (3.3) \\
4 \text{CO} + 8 \text{H}_2 & \rightleftharpoons \text{C}_4\text{H}_9\text{OH} + 3 \text{H}_2\text{O} & \text{Butanol} & (3.4) \\
n \text{CO} + 2n \text{H}_2 & \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1) \text{H}_2\text{O} & \text{any alcohol} & (3.5)
\end{align*}
\]

The main side reactions are formation of hydrocarbons, normally dominated by methane (eq. 3.6) together with short paraffins and olefins. Oxygenated by-products such as aldehydes,
esters and ethers might also be formed depending on catalyst and operation conditions used.

\[
\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad (3.6)
\]

The water-gas shift (WGS) reaction (eq. 3.7) occurs simultaneously with catalysts having water-gas shift activity.

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ_{298K} = -41.1 \text{ kJ/mol} \quad (3.7)
\]

The WGS equilibrium constant is large under the temperatures applied in higher alcohol synthesis, e.g. \(K_{330^\circ\text{C}}=26.8, K_{370^\circ\text{C}}=16.7\) \([31, 32]\). When the catalyst has high water-gas shift activity, this means that most of the water produced in the alcohol synthesis (eqs. 3.2-3.5) is converted together with CO in the water-gas shift reaction to \(\text{CO}_2\) and \(\text{H}_2\) (eq. 3.7). As an example, in the temperature range 330-370°C, 96.4-94.4% of the produced water is converted to \(\text{CO}_2\) if the \(\text{H}_2/\text{CO}=1\). The MoS\(_2\)-based catalysts covered in this thesis are of this type, displaying very high WGS activity.

This leads us to the definition of \(\text{H}_2/\text{CO}\) usage ratio which is the \(\text{H}_2\) per \(\text{CO}\) consumed to form a product e.g. ethanol. Four \(\text{H}_2\) and two \(\text{CO}\) are consumed in the formation and ethanol (and water) (eq. 3.2) i.e. the \(\text{H}_2/\text{CO}\) usage ratio is two. This is the usage ratio over a catalyst without water-gas shift activity. However, if the ethanol instead is formed over a catalyst with very high water-gas activity, both the ethanol formation reaction (eq. 3.2) and the water-gas shift reaction (eq. 3.7) occur simultaneously resulting in eq. 3.8 and the usage ratio becomes very close to one.

\[
2\text{ CO} + 4\text{ H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \quad \text{H}_2/\text{CO} \text{ usage ratio}=2 \quad (3.2)
\]

\[
3\text{ CO} + 3\text{ H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{CO}_2 \quad \text{H}_2/\text{CO} \text{ usage ratio}=1 \quad (3.8)
\]
The effect of the water-gas shift reaction on the H$_2$/CO usage ratio for the most important reaction products is displayed in table 3.1. For higher alcohol synthesis catalysts having water-gas shift activity this means that the feed syngas can have a lower H$_2$/CO.

Table 3.1. The effect of the water-gas shift reaction on H$_2$/CO usage ratio for the displayed products.

<table>
<thead>
<tr>
<th>Product</th>
<th>$\text{H}_2$/CO usage ratio without water-gas shift</th>
<th>$\text{H}_2$/CO usage ratio with water-gas shift $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Propanol</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>Butanol</td>
<td>2</td>
<td>0.71</td>
</tr>
<tr>
<td>Methane</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ assuming all H$_2$O formed is converted.

3.2 Catalysts, product distribution and developed processes

Presently, higher alcohols synthesis is not applied anywhere in the world on an industrial scale. A handful conceptual processes based on patented catalytic technologies have been developed and tested in industrial plants, pilot plants or extensively tested in bench scale reactors. The catalysts used in these processes are based on the main HAS catalyst families shown in Table 3.2, giving very different alcohol product distributions.
Table 3.2. Important types of higher alcohol catalysts

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Catalyst composition</th>
<th>Product composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT methanol (^a)</td>
<td>ZnCrO, MnCrO, ZnMnCrO + alkali</td>
<td>MeOH + i-BuOH (^b)</td>
</tr>
<tr>
<td>LT methanol (^a)</td>
<td>Cu/ZnO, Cu/ZnO/M(_2)O(_3) (M=Al, Cr) + alkali</td>
<td>(EtOH+PrOH)</td>
</tr>
<tr>
<td>Molybendum-based</td>
<td>e.g. MoS(_2), Ni-MoS(_2), Co-MoS(_2), MoC + alkali</td>
<td>straight-chain (^c)</td>
</tr>
<tr>
<td>MeOH + FT element</td>
<td>Cu-Co, Cu-Ni + alkali</td>
<td>C(_1)-C(_5) alcohols</td>
</tr>
<tr>
<td>Rhodium-based</td>
<td>e.g. Li-Mn-Rh, Rh-ZrO(_2)</td>
<td>C(_2) oxygenates (^d)</td>
</tr>
</tbody>
</table>

\(^a\) HT=high temperature, LT=low temperature  
\(^b\) branched primary alcohols, especially isobutanol in addition to methanol together with a smaller amount ethanol and propanol.  
\(^c\) straight primary alcohols with a composition resembling the Anderson-Schulz-Flory (ASF) distribution.  
\(^d\) acetaldehyde, ethanol and acetates [33].

Information regarding these processes, such as process name, catalyst composition and operating conditions can be found in Table 3.3 while representative alcohol distributions under these conditions are presented in Table 3.4. Changes in operation conditions such as temperature, gas hourly space velocity (GHSV) and syngas composition together with changes in catalyst composition can, however, greatly change these product distributions. A remarkable and unifying feature of most HAS catalysts is the presence of an alkali promoter, either to achieve higher alcohol selectivity or to stimulate higher alcohol selectivity.
<table>
<thead>
<tr>
<th>Process name</th>
<th>Catalyst</th>
<th>Catalyst type (promoted)</th>
<th>Temp. (°C)</th>
<th>Pressure (MPa)</th>
<th>H₂/CO-ratio</th>
<th>GHSV (h⁻¹)</th>
<th>Development stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAS (SEHT)b</td>
<td>K-Zn-Cr (Cu)</td>
<td>Modified HT methanol</td>
<td>330-430</td>
<td>9-18</td>
<td>0.5-3</td>
<td>3000-15000</td>
<td>Industrial plant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1982-1987 (15000 ton/year)</td>
</tr>
<tr>
<td>Octamix (Lurgi)c</td>
<td>K-Cu-Zn-Al</td>
<td>Modified LT methanol</td>
<td>250-300</td>
<td>6-10</td>
<td>1</td>
<td>400-6000</td>
<td>Pilot plant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(730 ton/year)</td>
</tr>
<tr>
<td>Substifuel (IFP)e</td>
<td>K-Cu-Co-Al, K-Cu-Ni-Ti</td>
<td>MeOH &amp; FT element</td>
<td>280-320</td>
<td>6-10</td>
<td>1.2-1.8</td>
<td>3000-6000</td>
<td>Pilot plant</td>
</tr>
</tbody>
</table>

\[a\] Process development company displayed within brackets

\[b\] Metanolo piu Alcoli Superiori (MAS) developed by Snamprogetti, Enichem and Haldor Topsøe (SEHT)

\[c\] Lurgi and Süd Chemie

\[d\] Dow Chemicals and Union Carbide

\[e\] Institut du Français du Pétrole (IFP) with Idemitsu Kosan (IK)
Table 3.4. Alcohol composition from syngas [38]

<table>
<thead>
<tr>
<th>Process</th>
<th>Alcohols (%)</th>
<th>Other oxyg.</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₁</td>
<td>C₂</td>
<td>C₃</td>
</tr>
<tr>
<td>MAS (SEHT)</td>
<td>69</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Octamix (Lurgi)</td>
<td>62</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>HAS (Dow)</td>
<td>26</td>
<td>48</td>
<td>14</td>
</tr>
<tr>
<td>Subsifuel (IFP)</td>
<td>64</td>
<td>25</td>
<td>6</td>
</tr>
</tbody>
</table>

ᵃ branched alcohols are in majority; 70% of the C₄ alcohols are isobutanol in Octamix.
ᵇ mainly straight alcohols.

3.3 Thermodynamics for higher alcohol synthesis

In order to understand the equilibrium limits imposed in higher alcohol synthesis, i.e. conversion of syngas to alcohols and hydrocarbons, a thermodynamic analysis was made. The calculations were performed with Aspen plus software using the Gibbs free energy minimization module entitled RGIBBS and the Soave-Redlich-Kwong (SRK) equation of state.

Reflecting the fact that conversion of syngas to alcohols and hydrocarbons is highly exothermic and proceeds with volume contraction, their formation is thermodynamically favored by low temperature and high pressure (seen for ethanol in Fig. 3.1). As the chain length of the alcohols increases they become more favored thermodynamically. In Fig. 3.3 this is demonstrated, the equilibrium composition for the three shortest alcohols from syngas was calculated at different temperatures. This also means that higher temperatures can be applied before the syngas conversion is limited by equilibrium for longer alcohols than for shorter ones (compare EtOH, Fig. 3.1 lower, with MeOH, Fig. 3.2). Nevertheless, formation of methane and other hydrocarbons is preferred thermodynamically over alcohol formation from syngas (Fig. 3.4 compares ethanol and methane). Therefore hydrocarbon
Fig. 3.1. Equilibrium mol fraction (left) and equilibrium carbon fraction (right) as function of temperature for ethanol. This is shown for three different total pressures, 1 bar (top), 10 bar (middle) and 100 bar (bottom). A syngas gas with H\textsubscript{2}/CO\textsubscript{2}=1 inlet ratio has been used in the calculations and possible products have been set to ethanol, CO\textsubscript{2} and H\textsubscript{2}O.
Fig. 3.2. Equilibrium mol fraction (left) and equilibrium carbon fraction (right) as function of temperature when methanol formation is allowed. $P_{\text{tot}}=100$ bar and $H_2/CO=1$ inlet ratio (methanol formation is limited by $H_2$ concentration).

Fig. 3.3. Equilibrium mol fraction (left) and equilibrium carbon fraction (right) as function of temperature when propanol formation, in addition to methanol, ethanol, CO$_2$ and H$_2$O, is allowed. $P_{\text{tot}}=100$ bar and $H_2/CO=1$ inlet ratio.

Fig. 3.4. Equilibrium mol fraction (left) and equilibrium carbon fraction (right) as function of temperature when methane formation in addition to ethanol, CO$_2$ and H$_2$O is allowed. $P_{\text{tot}}=100$ bar and $H_2/CO=1$ inlet ratio.
formation must be kinetically limited, meaning that a good alcohol catalyst must impose a kinetic barrier to their formation while at the same time catalyzing alcohol formation.

Arranging the main products from the most to the least thermodynamically favorable products the chart become as follows:

CH₄ > paraffin > i-BuOH > n-BuOH > n-PrOH > EtOH > MeOH

3.4 Higher alcohol synthesis, a historical resume

For more than a century it has been known that longer alcohols can be produced from syngas. In 1913 BASF patented a process for syngas conversion into a mixture containing hydrocarbons, alcohols, aldehydes, ketons, acids and other organic compounds using e.g. an alkalized cobalt and osmium oxide catalyst [39]. A big step forward was achieved by Fischer and Tropsch in the early 1920’s when they developed the Synthol process (not to be confused with the SASOL Synthol process), which had a much higher alcohol selectivity [25, 26, 40, 41]. The reaction was performed over an alkalized iron catalyst at 100-150 bar and 400-450 °C, resulting in a mixture containing mainly of alcohols, hydrocarbons, aldehydes and ketones [40, 41].

Soon after BASF discovered the ZnO/Cr₂O₃ catalyst for synthesis of methanol in 1923, it was found that alkali addition to the catalyst gave high yields of higher alcohols in addition to ethanol. From 1927 to 1945, plants of this type were in operation in the USA and Germany [34]. In the time period 1935-1945 direct synthesis of higher alcohols assumed considerable importance in Europe [42]. A modified Synthol process was developed by I.G. Farbenindustrie from 1940-1945 in which much lower reaction temperature (190-200 °C) and greater gas recycle, then the
original method was applied [43]. Higher alcohol selectivity could in this way be achieved, while the rest of the product mainly consisted of olefins and paraffins. A German plant, producing 10-15 ton/month of liquid product was under construction in the end of the Second World War, but was never completed after bombardment in the end of the war [43]. The accessibility of cheap oil e.g. due to the exploration of the Arab oilfields and a demand for pure alcohols for chemical use, made the interest for higher alcohols and other synthetic fuels cease in the time period after the war.

The interest in HAS thereafter has been renewed in times of high (or expected high) oil prices and uncertainties regarding energy supply. In the 1970’s and 1980’s there was an intensive world-wide research effort on the production and use of synthesis gas derived from coal as an alternative to crude oil for production of synthetic fuels. The Arab oil embargo (1973), the Iranian revolution (1979) and the start of the Iran/Iraq war (1980) spurred this development, and displayed the Western countries’ heavy dependence on Middle East oil and vulnerability of such an energy supply chain. It is at this time virtually all of the most interesting catalytic systems of today were developed or older methods refined and improved.

Greatly declined oil prices in the mid-80’s, diminished the economic and political incentives, and focus switched towards the environmental benefits of alcohol addition to gasoline. Mixing alcohols with gasoline was seen as a way to reduce local air pollution (e.g. CO and ozone) and alcohol’s excellent anti-knock properties a method to help phasing out or reduce environmentally questionable octane enhancers such as alkyl-lead, aromatic hydrocarbons (e.g. benzene) and MTBE (methyl tert-butyl ether).

In the early 21st century HAS saw a revitalized interest from industry and academia with attention on reducing greenhouse gas emissions and foreign oil dependence due to increased and anticipated increase in petroleum prices. While the research in
most Western countries are concentrated around on using biomass as raw material, available coal is the center of attention in China. The world economic slowdown together with a reduced oil price has to some extent reduced the interest in HAS during the last few years.
Chapter 4

Alcohol fuels for internal combustion engines

4.1 Fuel properties

Alcohols have fuel properties suitable for use in combustion engines. They can be used either neat or blended in different portions with gasoline for use in spark-ignition engines. In addition hydrous alcohols can be used in specially designed compression-ignition (diesel) engines if a small amount of ignition improver is added to the fuel [44].

The octane rating is a measure of the fuel’s ability to resist auto-ignition and knock, and is therefore a critical fuel property affecting the design, operation and efficiency of spark-ignited engines. All alcohols display very high octane numbers compared to gasoline which makes them very attractive for use either pure or as gasoline octane enhancer. In Table 4.1 octane number and other significant fuel properties for a number of alcohols in comparison with gasoline are shown. Alcohols display higher octane rating and evaporative cooling (see heat of vaporization in Table 4.1) compared to gasoline which enables an increase in the engine’s compression ratio without running into problems with pre-ignition and knock [45]. Increasing the compression ratio is of great benefit for overall efficiency, fuel consumption and CO₂ emissions [46]. Dedicated alcohol engines, optimized to running on alcohol (or gasoline with high blending portions of alcohols) therefore would make it possible to create much more efficient engines, which is not possible with the currently used “alcohol cars” so called Flex-fuel Vehicles (FFV), running on both alcohol and gasoline [45].
Adding alcohol(s) to gasoline increases the blended fuel’s octane number much more than predicted from the volume alcohol added and the individual octane numbers of the alcohol and the gasoline from which it is produced [47, 48]. This is the property called blend octane number (Table. 4.1).

The octane number of the alcohols decreases with increased alcohol chain length while the energy density increases. However, compared to gasoline the energy density of alcohols is significantly lower (Table 4.1). Mixing pure methanol with gasoline is often not preferred; since there is a risk of phase separation if water enters the fuel system (water and methanol separate from hydrocarbons). This problem can, however, easily be solved by co-adding other longer alcohols to stabilize the blend [48].

Appropriate volatility of the alcohols-gasoline blend is also important to avoid vapor lock problems in regions with high temperatures and cold start problems when the temperature is low in colder areas. Despite the low vapor pressures of neat alcohols, addition of methanol or ethanol to gasoline results in a substantial increase in the vapor pressure of the fuel (Table 4.1). This happens because a positive azeotropic mixture is formed when alcohols and hydrocarbons are mixed, a mixture which has lower boiling point than the hydrocarbons and alcohols from which it is made [49]. Adding small quantities of methanol or ethanol to the fuel blend (<1%) increases the fuel vapor pressure greatly [50]. Further addition in the range of 1%-15% alcohol does not change the vapor pressure significantly, while higher concentrations lead to its gradual reduction [50, 51].
Table 4.1. Important fuel properties of various short alcohols and gasoline [48, 51-53].

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Gasoline</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>1-propanol</th>
<th>1-butanol</th>
<th>1-pentanol</th>
<th>i-PrOH</th>
<th>i-butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat - Research octane number, RON</td>
<td>91-99</td>
<td>109</td>
<td>108</td>
<td>105</td>
<td>98</td>
<td>86</td>
<td>112</td>
<td>105</td>
</tr>
<tr>
<td>Neat - Motor octane number, MON</td>
<td>81-89</td>
<td>89</td>
<td>88</td>
<td>88</td>
<td>85</td>
<td>76</td>
<td>97</td>
<td>89</td>
</tr>
<tr>
<td>Blend octane values - RON</td>
<td>-</td>
<td>127-136</td>
<td>120-135</td>
<td>94-96</td>
<td>120</td>
<td>113</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blend octane values - MON</td>
<td>-</td>
<td>99-104</td>
<td>100-106</td>
<td>78-81</td>
<td>96</td>
<td>94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen content (wt%)</td>
<td>0-4</td>
<td>49.9</td>
<td>34.7</td>
<td>26.6</td>
<td>21.6</td>
<td>18.1</td>
<td>26.6</td>
<td>21.6</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>38-204</td>
<td>64.7</td>
<td>78.3</td>
<td>97.2</td>
<td>117.7</td>
<td>138</td>
<td>82.3</td>
<td>107.9</td>
</tr>
<tr>
<td>Stoichiometric air/fuel ratio (wt/wt)</td>
<td>14.7</td>
<td>6.46</td>
<td>8.98</td>
<td>10.33</td>
<td>11.17</td>
<td>11.73</td>
<td>10.33</td>
<td>11.17</td>
</tr>
<tr>
<td>Heat of vaporization (MJ/l)</td>
<td>0.20-0.28</td>
<td>0.93</td>
<td>0.73</td>
<td>0.63</td>
<td>0.57</td>
<td>0.53</td>
<td>0.58</td>
<td>0.55</td>
</tr>
<tr>
<td>Neat - vapor pressure (kPa) a</td>
<td>55-65</td>
<td>32</td>
<td>16</td>
<td>6.2</td>
<td>2.2</td>
<td>12.4</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Mix - vapor pressure (kPa) a,b</td>
<td>-</td>
<td>84</td>
<td>68</td>
<td>60</td>
<td>59</td>
<td>62</td>
<td>59</td>
<td></td>
</tr>
</tbody>
</table>

a Reid vapor pressure (RVP) at 37.8 °C.

b mixture containing: 10% (v/v) alcohol and 90% gasoline. Gasoline vapor pressure (RVP) was 60 kPa.
4.2 Alcohols as motor fuel is not new

The idea of using alcohols to fuel vehicles is as old as the car industry itself. Automobile pioneer Henry Ford’s first produced car in 1896 (the Quadricycle) was made to run on pure ethanol, and one of the most influential cars ever built, the Ford model T (1908-1927) was designed to run on either ethanol, kerosene or gasoline [54]. In a New York Times interview in 1925 Ford called ethanol, “the fuel of the future”, a view that was widely shared in the automotive industry of the time [55]. The decreasing cost of gasoline and the discovery of tetra ethyl lead as an octane booster were some of the factors hindering the alcohol industry’s growth and gasoline took over [56].

4.3 Legislation and current use of alcohols

Ethanol is the mainly used fuel alcohol and ethanol-gasoline blends are available in a great number of nations over the world. United states and Brazil are the main fuel ethanol-producing countries, with where corn and sugar cane as raw materials, respectively, being fermented to ethanol [57].

In Brazil there is a widespread use of cars running on 100% hydrous ethanol (E100) and a 25% ethanol addition to gasoline is mandatory (E25) [58].

So called flex-fuel vehicles, developed to run on both E85 and gasoline with less or no ethanol added are available in e.g. the USA, Brazil and some European countries.

However, the vast majority of the ethanol produced is blended lower concentration in gasoline for used in standard gasoline cars. The blend concentration mainly lies between 4 and 10% ethanol.

In the USA, ethanol accounted for about 10% of the total volume of finished motor gasoline consumed in 2013 [59]. Most sold gasoline in the US contains some ethanol and 10% ethanol in
gasoline (v/v) is mandated in numerous states. Other offered ethanol-gasoline blends on the US market are, E15 for newer gasoline vehicles (from the year 2001) and E85 for Flex-Fuel vehicles [59].

Blending 4-5% ethanol into gasoline is mandatory in several European countries, while blends up to 10% ethanol are allowed according to legislation [60].

European Union regulation for ethanol, methanol and other short alcohols for use in gasoline are presented in Table 4.2 [60]. Also unspecified alcohols are allowed up to the concentrations stated under the general oxygenate group, as long as the total oxygen content does not exceed 2.7 wt% oxygen and other parts of the fuel standard is met, e.g. regarding fuel volatility.

It has long been known that alcohols are suitable fuels for spark ignition engines, but it was not until the 80’s engines operating according to the diesel principle were developed for methanol and ethanol fuels (with addition of ignition improver) [50]. For use in specially developed diesel engines, the ED95 fuel was developed. ED95 consists of 95% hydrous ethanol together with 5% ignition improver (polyethylene glycol) and is sold for used in specially developed diesel engines in a dozen countries [61]. In Sweden over 800 Scania busses are running on ED95 [62].

Methanol was for a long time mainly used in high-performance engines, e.g. in Grand Prix racing vehicles in the 1930’s and in the Indianapolis 500 racing series during the period 1964-2006, but not in ordinary cars. After the 70’s oil crises, the interest in methanol became intense and it was seen as the most probable gasoline substitute and gasoline extender, for use in ordinary cars [44]. Today, the main user and producer of fuel methanol is China, where M15 represents 8% of the gasoline fuel pool and it continues to grow [21]. The Chinese methanol is mainly produced from gasification of domestic coal and its use has risen rapidly since it can be produced at a low cost, has clean-burning properties and can increase the nation’s energy security [63].
Australia, Israel and Iceland are other countries with increasing interest and use of methanol in gasoline.

Table 4.2. Motor-gasoline specification and legislation in the European Union [60]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>Research octane number</td>
<td>95</td>
<td>—</td>
</tr>
<tr>
<td>Motor octane number</td>
<td>85</td>
<td>—</td>
</tr>
<tr>
<td>Oxygen content</td>
<td>% m/m</td>
<td>3.7</td>
</tr>
<tr>
<td>Oxygenates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>— Methanol</td>
<td>% v/v</td>
<td>— 3.0</td>
</tr>
<tr>
<td>— Ethanol</td>
<td>% v/v</td>
<td>— 10.0</td>
</tr>
<tr>
<td>— Iso-propyl alcohol</td>
<td>% v/v</td>
<td>— 12.0</td>
</tr>
<tr>
<td>— Tert-butyl alcohol</td>
<td>% v/v</td>
<td>— 15.0</td>
</tr>
<tr>
<td>— Iso-butyl alcohol</td>
<td>% v/v</td>
<td>— 15.0</td>
</tr>
<tr>
<td>— Ethers (containing five or more carbon atoms)</td>
<td>% v/v</td>
<td>— 22.0</td>
</tr>
<tr>
<td>— Other mono-alcohols and ethers b</td>
<td>% v/v</td>
<td>— 15.0</td>
</tr>
<tr>
<td>Hydrocarbon analysis:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>— olefins</td>
<td>% v/v</td>
<td>— 18.0</td>
</tr>
<tr>
<td>— aromatics</td>
<td>% v/v</td>
<td>— 35.0</td>
</tr>
<tr>
<td>— benzene</td>
<td>% v/v</td>
<td>— 1.0</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>mg/kg</td>
<td>— 10.0</td>
</tr>
<tr>
<td>Lead content</td>
<td>g/l</td>
<td>— 0.005 c</td>
</tr>
<tr>
<td>Distillation:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>— percentage evaporated at 100 °C</td>
<td>% v/v</td>
<td>46 —</td>
</tr>
<tr>
<td>— percentage evaporated at 150 °C</td>
<td>% v/v</td>
<td>75 —</td>
</tr>
</tbody>
</table>

a Test methods shall be those specified in EN 228:2004
b Other mono-alcohols and ethers with a final boiling point no higher than that stated in EN 228:2004
c No intentional addition allowed
Chapter 5

Higher alcohol synthesis with molybdenum sulfide catalysts

5.1 General

In conversion of syngas to organic products, non-promoted MoS$_2$ catalysts display selectivity to methane and other short hydrocarbons [64], however, as first revealed by Dow Chemicals [65] and Union carbide [66], when the MoS$_2$ is promoted with alkali and pressure applied, high selectivity to mixed alcohols can be achieved. Doping the MoS$_2$ with alkali is therefore crucial for obtaining alcohols rather than hydrocarbons. Mainly linear primary alcohols are produced with alkali/MoS$_2$ catalysts, while the dominant side products are short hydrocarbons, in particular methane. Group VIII promoters such as nickel or cobalt are often added to the catalyst in order to shift the product distribution towards longer alcohols [67-70]. Even if the sulfide (MoS$_2$) is the most studied and preferred state of the alkali/Mo catalyst, also carbide, oxides, phosphides and the metallic form of the catalyst have been shown to have HAS activity [65, 68, 71]. Molybdenum sulfide can be prepared from both oxide and sulfide precursors, but higher HAS activity is reported from sulfide precursors [65]. Unsupported molybdenum sulfide is the preferred state of the catalyst in the patent literature, however, the active material may also be placed on suitable carrier materials e.g. carbon, Al$_2$O$_3$ or SiO$_2$ [65]. At a given temperature alcohol selectivity increases with increasing pressure, however, the costs associated with carrying out the reaction at increased pressures also increase [65].
Improved alcohol selectivity at higher pressure must therefore be balanced against rising costs associated with pressure vessels, compressors and energy use.

A significant difference compared to many other HAS catalytic systems is that the methanol concentration with MoS$_2$-based catalysts is as a rule not limited by thermodynamic equilibrium under normal operation conditions, meaning that the methanol formation rate is fairly slow.

Molybdenum sulfide-based catalysts (promoted with Ni or Co on an Al$_2$O$_3$ support) are being used at huge scale for cleaning petroleum streams from sulfur (hydrodesulfurization) in the production of fuels in the oil refining industry [72]. Due to hydrodesulfurization’s very great strategic importance in today’s oil-dependent society, molybdenum sulfide catalysts of this type are among the most studied and best described heterogeneous catalysts. However, the knowledge on hydrodesulfurization catalysts is hard to apply in HAS because of the essential role of alkali and the different reactions taking place on the catalyst.

Water-gas shift catalysts based on MoS$_2$ are commercially available for use when the gas contains sulfur and the syngas has a low H$_2$/CO ratio (low H$_2$O/C feed ratio) [5, 73, 74]. In addition, recently increased attention has been directed towards MoS$_2$ as a sulfur and coke tolerant CO methanation catalyst converting syngas derived from coal to methane [75].

### 5.2 Structure of MoS$_2$

MoS$_2$ is a layered compound, where each layer consists of a slab of Mo atoms sandwiched between two slabs of sulfur atoms (S-Mo-S layer). Molybdenum (Mo$^{4+}$) is coordinated to six sulfur ligands (S$^2-$) in a trigonal prismatic configuration and the layers are held together by van der Waals forces leading to a more or less stacked organization of MoS$_2$ slabs (Fig. 5.1). These give MoS$_2$ an
appearance and feel similar to graphite, while the material’s robustness and low friction properties make it a well-used lubricant.

Worth to notice is that the slabs of industrially used MoS₂-based catalysts are often not flat and perfect, but poorly crystalline, exhibiting a disordered bent morphology [76].

Nanoparticulate MoS₂ has, in addition to layered structures, been found to form fullerene and nanosphere microstructures [76, 77]. MoS₂ can also host intercalation compounds, in which the host atoms or molecules are located in the van der Waals gap between the MoS₂ slabs [78-80]. A typical compound of this type is LiₓMoS₂ [80].

Fig. 5.1. Crystal structure of molybdenum sulfide (2H-MoS₂) and its typical layered structure. Molybdenum and sulfur are illustrated in red and yellow, respectively. Relative atom positions in the MoS₂ single layer are clarified in the upper-right figure, while their positions relative the second layer are illustrated in the lower-right figure.
5.3 Alkali and group VIII promoters

Doping the MoS$_2$ with alkali is essential for obtaining a catalyst that will produce alcohols rather than hydrocarbons. Alkali tunes kinetics and energetics of the adsorbed reactants thereby affecting their relative coverage during reaction. More precisely, alkali has been postulated to activate CO non-dissociatively and reduce the availability of activated hydrogen on MoS$_2$, thereby favoring synthesis of higher alcohols over hydrocarbons [69].

There are different reports regarding which alkali metal is the most suitable one, but the heavier Cs, Rb, K are very much preferred over the lighter Na, Li [71, 81-83]. The optimum alkali level is fairly high, alkali/Mo-molar ratios in the range 0.1-0.7 have in general been applied [71, 84]. An increased alkali level appears to be needed at higher reaction temperatures and greater MoS$_2$ surface areas for maximum alcohol productivity [71, 81]. Alkali addition favors alcohol selectivity over that to hydrocarbon, while excessive addition leads to a reduced alcohol productivity [81].

Successful alkali promotion can however not be performed with any alkali salt. Woo and Lee studied the promotion of MoS$_2$ with different potassium precursors and found the correct choice essential for achieving catalysts with high alcohol selectivity [85, 86]. Successful precursors were able to remove their anion and spread on the MoS$_2$ surface under reaction conditions, while the opposite was found true for the bad precursors. Suitable choices were found to be e.g. K$_2$CO$_3$, K$_2$O$_2$, K$_2$S, while poor promotion abilities were seen for KCl and K$_2$SO$_4$.

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The alkali promoter can be added by either conventional impregnation or physical mixing. Both methods appear equally good in the case of K$_2$CO$_3$ promoter, since the activity and selectivity of the catalyst is the same independently of method used [86, 87]. Comparing alkali dispersion on a fresh catalyst with one already used for CO hydrogenation, much higher alkali dispersion is shown on the latter [85]. This indicates that the two alkali
addition methods are comparable since the alkali is highly mobile and therefore migrates and redistributes under reaction conditions, giving similar dispersion and therefore performance in the end. Support for this can also be found in the great change in activity and selectivity experienced during the first 5-30 hours on stream, often referred to as the induction period [87, 88]. During this time CO conversion decreases greatly while a simultaneous increase in alcohol selectivity and a drop in hydrocarbon selectivity is witnessed, which is typical for when alkali disperses on MoS$_2$ [85, 89].

Recent research by Santos shows that the induction period can be shortened if incipient wetness impregnation is used instead of physical mixture in the case of K$_2$CO$_3$ promoter. This might simply be related to a higher initial alkali dispersion in the former relative the latter [87]. They also found the results of K$_2$SO$_4$ promotion to be dependent on the preparation method used; incipient wetness impregnation gave good promoting effect, while physical mixing gave bad promoting effect, showing that the promotional effect not only depends on the precursor, but also on the way the alkali is incorporated.

Even if MoS$_2$ is fairly stable in air, prolonged storage of K$_2$CO$_3$/MoS$_2$ in normal atmosphere has been shown to partly oxide the catalyst (stored for 11 weeks) [86]. In this process some sulfide (S$^{2-}$) is converted to sulfate (SO$_4^{2-}$) and parts of the Mo$^{4+}$ to Mo$^{6+}$, leading to decreased alcohol selectivity and increased C$_2^+$ hydrocarbon production [86]. In order to sidestep catalyst degradation, minimum contact between the prepared catalyst and moist air therefore is advised, meaning inert atmosphere storage.
5.4 Reaction mechanism

The studies made in order to understand the product formation mechanisms over MoS$_2$-based catalysts are extremely few and basically limited to a study by Santiesteban [69]. However, it is known that co-feeding various alcohols (methanol, ethanol), aldehydes (acetaldehyde) and olefins (ethene, propene) under reaction conditions, they can all grow into longer alcohols and hydrocarbons [90-93]. DFT calculations indicate the pathway for methane formation on alkali-free MoS$_2$ (10-10 surface) to be as follows [94]. Observe that CO is adsorbed non-dissociatively.

\[
\text{CO} \rightarrow \text{CHO} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_3 \rightarrow \text{CH}_4 \quad (5.1)
\]

Methanol formation has in a similar way been proposed to be formed by direct CO hydrogenation [69]. Santiesteban et al. co-fed isotope-labeled methanol ($^{13}$CH$_3$OH) over a Cs-MoS$_2$ catalyst and found the produced alcohols to be $^{13}$C-enriched at the terminal carbon ($^{13}$CH$_3$CH$_2$OH, $^{13}$CH$_3$CH$_2$CH$_2$OH, $^{13}$CH$_3$CH$_2$CH$_2$CH$_2$OH) [69]. Chain growth therefore must have occurred by insertion of a carbon element derived from CO at the hydroxyl-carbon of the alcohol. Santiesteban proposed following mechanism:

\[
\begin{align*}
^{13}\text{CH}_3\text{OH}^* & \rightarrow^{13}\text{CH}_x\text{O}^* \rightarrow^{13}\text{CH}_x^* \\
^{13}\text{CH}_3\text{CH}_2\text{OH}^* & \leftarrow^{13}\text{CH}_3\text{CO}^* \rightarrow^{13}\text{CH}_3\text{CH}_2^* \\
^{13}\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^* & \leftarrow^{13}\text{CH}_3\text{CH}_2\text{CO}^* \rightarrow^{13}\text{CH}_3\text{CH}_2\text{CH}_2^*
\end{align*}
\]

Fig. 5.2. Proposed alcohol chain growth mechanism over Cs-MoS$_2$ catalyst.
However, identical experiments with a K-Co-MoS$_2$ catalyst at lower space velocity gave somewhat different results since two types of propanol in equal amounts were being produced, $^{13}$CH$_3$CH$_2$CH$_2$OH and CH$_3$CH$_3$CH$_2$OH, while the ethanol composition still was $^{13}$CH$_3$CH$_2$OH. Even if the results are a bit non-unifying, nothing points towards alcohol to alcohol coupling reactions.

Christensen et al., however, proposed an alternative chain growth route where alcohol-alcohol coupling reactions take place, based on that fact the butanol formation rate was increased much more than the propanol formation rate when increased amounts of ethanol were co-fed [91].

Methane and other hydrocarbons are at least partly expected to be produced from the corresponding alcohols, but to which extent this happens is quite unclear [69].

### 5.5 Anderson-Schulz-Flory (ASF) distribution

The alcohol product distribution from alkali-promoted MoS$_2$ catalysts as well as the hydrocarbon product distribution from alkali-free MoS$_2$ catalysts have often been deemed to approximately follow the so-called ASF (Anderson-Schulz-Flory) distribution [95]. Significant deviations from the ASF distribution are however often reported, especially for C$_1$ species when promoters such as Ni or Co are added [70, 96-98]. The ASF distribution is derived from polymerization kinetics with C$_1$ monomers and is valid when the probability of chain growth ($\alpha$) is independent of chain length [99, 100]. Regardless of the exact mechanism for carbon growth, this means that growth of the carbon chain occurs by a stepwise addition of a single-carbon segment derived from CO, and the probability of chain growth is independent on the length of the growing carbon chain. According to this model the product distribution can simply be described by a single parameter, the chain growth probability ($\alpha$). $\alpha$ is defined by:
\[ \alpha = \frac{R_p}{R_p+R_t} = \frac{k_p}{k_p+k_t} \]  \hspace{1cm} (5.2)

where \( R_p \) and \( R_t \) are the rates of propagation and termination, respectively, with \( R_p=k_p\theta_n \), \( R_t=k_t\theta_n \). \( k_p \) and \( k_t \) are the rate coefficients for propagation and termination, respectively, and \( \theta_n \) is the surface concentration of the chain with \( n \) carbon atoms. Consequently, the probability of chain termination becomes:

\[ 1-\alpha = \frac{R_t}{R_p+R_t} = \frac{k_t}{k_p+k_t} \]  \hspace{1cm} (5.3)

The distribution can mathematically be represented in the following way:

\[ S_n = n \cdot (1-\alpha)^2\alpha^{n-1} \]  \hspace{1cm} (5.4)

where \( S_n \) is the carbon selectivity for chains with \( n \) carbon atoms and \( \alpha \) is chain growth probability. A plot of \( \ln \left( \frac{S_n}{n} \right) \) vs. \( n \) (ASF plot) gives a straight line when the chain growth probability (\( \alpha \)) is independent of \( n \).

\[ \ln \left( \frac{S_n}{n} \right) = n \ln \alpha + \ln \left( \frac{(1-\alpha)^2}{\alpha} \right) \]  \hspace{1cm} (5.5)

In higher alcohol synthesis, a number of different product groups are usually formed, e.g. alcohols, aldehydes, olefins and paraffins. Fig. 5.3 shows a chain growth model for formation of paraffins and alcohols from a common intermediate. If the termination probability ratio between hydrocarbons and alcohols \( \left( \frac{R_t_{Alc}}{R_t_{HC}}=\frac{k_{t_{Alc}}}{k_{t_{HC}}} \right) \) is constant and independent of chain length, the hydrocarbon and alcohol ASF plots will be copies of each other only differing by an y-axis offset. The termination probabilities for
hydrocarbons and alcohols then become \( \frac{k_{tHC}}{k_p + k_{tHC} + k_{tAlc}} \) and \( \frac{k_{tHAlc}}{k_p + k_{tHC} + k_{tAlc}} \), respectively, and the y-axis offset in the ASF plot will reflect the difference in magnitude of the chain termination probabilities. Chain growth through a common intermediate to more than two products can be viewed in an equivalent way.

Fig. 5.3. Chain growth to paraffins and alcohols through a common intermediate.
Chapter 6

Catalyst preparation and characterization

This chapter starts with describing preparation routes for synthesizing MoS$_2$-based catalysts. A description of the synthesis and characterization of the catalysts used in this work then follows.

6.1 Catalysts preparation routes

Two main routes for synthesizing MoS$_2$ catalysts exist; sulfidation of molybdenum oxide and decomposition of molybdenum-sulfur material or salt containing over-stoichiometric amounts of sulfur, e.g. MoS$_4^{2-}$ or MoS$_3$. The catalysts prepared in this thesis are examples of the latter method.

6.1.1 Decomposition of sulfur-molybdenum compounds

In the decomposition method, the MoS$_2$ precursor has sulfur bonds to molybdenum and some of the over-stoichiometric sulfur is lost during decomposition. A typical example is decomposition of ammonium tetrathiomolybdate (ATTM), (NH$_4$)$_2$MoS$_4$, as shown in eq. 6.1 [101].

\[
(NH_4)_2MoS_4 \xrightarrow{\Delta} 2NH_3 + H_2S + (3-x)S + MoS_x \quad (x=2-3) \]  

(6.1)

Decomposition of thiosalts and molybdenum-sulfur materials in this way leads to more sulfided catalysts compared to the conventional sulfidation of molybdenum oxides. The sulfur-to-
molybdenum ratio might even be above 2, as seen in the decomposition scheme above.

6.1.2 Sulfidation of MoO₅

The conventional way of preparing hydrotreating catalysts is an example of the metal oxide sulfidation method. Mo and Co or Ni salts are impregnated onto γ-Al₂O₃, followed by calcination to produce the stable oxidic material. The oxide is then sulfided either prior to or during the start-up of the hydrotreating process by passing sulfur-containing gas together with hydrogen over the catalyst. Sulfidation of the oxide(s) in this way is usually difficult and does not proceed in a regular manner, making the sulfidation process somewhat incomplete [102, 103].

6.2 Preparation of K-Ni-MoS₂ and MoS₂ catalysts

A summary of the preparation procedures used for synthesizing the catalysts used in the present work will follow. Two catalyst types were prepared, a promoted MoS₂ catalyst (K-Ni-MoS₂) and a “pure” MoS₂ catalyst. Additional details are available in Paper II.

The alcohol synthesis catalyst (K-Ni-MoS₂) was prepared from two water solutions; the first solution contained ammonium tetrathiomolybdate, ((NH₄)₂MoS₄) and the second nickel acetate, both in quantities equivalent to 47 mmol. The nickel acetate solution was added dropwise to the (NH₄)₂MoS₄ solution under strong agitation, and a black suspension was immediately formed as nickel reacted with thiomolybdate (eq. 6.2).

\[
\text{Ni}^{2+} (\text{aq}) + \text{MoS}_4^{2-} (\text{aq}) \rightarrow \text{NiMoS}_4 (\text{s}) \quad (6.2)
\]
After have been matured for 1 h under agitation the catalyst precursor (NiMoS₄) was washed, and centrifuged to remove excess liquid. The precursor was dried and thereafter crushed and sieved to a pellet size of 45-200 µm. Finely ground K₂CO₃ was then mechanically mixed with the "Ni-MoS₄" catalyst precursor and calcined/decomposed in a tube furnace at 450 °C for 90 min under flowing H₂ atmosphere. During this process a great amount of sulfur is removed from the catalyst both as elemental sulfur and as hydrogen sulfide.

The non-promoted MoS₂ catalyst was prepared by decomposition of ammonium tetrathiomolybdate (NH₄)₂MoS₄ at 500 °C and 45 h under flowing H₂ atmosphere (eq. 6.1).

6.3 Catalyst characterization

The catalyst characterization results for the studied catalysts are summarized here. For basic understanding of the applied characterization techniques the reader is directed to the relevant literature, e.g. in catalyst characterization or the specific methods. For details on the instruments, sample preparation, analysis conditions, and more in depth discussion of the results, the experimental sections of Papers II and III are advised.

6.3.1 N₂ physisorption and ICP-MS

N₂ physisorption (adsorption) at the boiling point of liquid nitrogen (~196 °C) was used to study the catalysts’ surface area (BET surface area), pore volume and pore distribution [104, 105]. Due to the low specific surface area of the studied catalysts (Table 6.1), great sample quantities were needed for achieving accurate analytical results [106]. The recommendation of keeping
the total surface area above 40 m² (40-120 m²) from the instrument manufacturer was followed [106].

Quantitative element analysis was performed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) after the catalyst has been completely dissolved in acid (HCl and HNO₃) and thereafter diluted with water.

The investigated catalysts’ physical properties found from N₂ physisorption and ICP-AES measurements are presented in Table 6.1. The metal ratios (K/Ni and Ni/Mo) were the ones aimed for and the BET surface areas are low. Also notice the magnitude of the S/Mo-ratio, sulfur has been removed from the precursor material (as anticipated) but still fairly high levels are present, displaying that probably also Ni (or NiMo) in addition to Mo holds a large amount of sulfur.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N₂ physisorption</th>
<th>ICP (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET (m²/g)</td>
<td>Avg. pore diameter (Å)</td>
</tr>
<tr>
<td>K-Ni-MoS₂</td>
<td>3.3</td>
<td>329</td>
</tr>
<tr>
<td>MoS₂</td>
<td>8.6</td>
<td>238</td>
</tr>
</tbody>
</table>

6.3.2 X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) was used for crystal phase identification, deduction of unit cell dimensions and crystallite size determinations. The diffractograms of the promoted and non-promoted catalysts both display typical MoS₂ patterns (Fig. 6.1). However, for the promoted catalyst the most intense peak is shifted somewhat towards a lower angle (2θ=13.8) compared to well-ordered and crystallized MoS₂ (2θ=14.4°). The increased distance between the MoS₂ sheets (expansion of the c lattice
parameter) (Table 6.2) has been explained to originate from curved layers where interlayer expansion occurs due to a mechanism for strain relief [107, 108]. For the promoted catalyst another MoS$_2$ layered phase is in addition formed, K$_x$MoS$_2$(H$_2$O)$_y$. This is a K$_x$MoS$_2$ phase which prior to XRD analysis has been

Fig. 6.1. XRD patterns for the MoS$_2$ (blue) and K-Ni-MoS$_2$ (black) catalysts. For comparison K-MoS$_2$ (green) and Ni-MoS$_2$ (red) prepared materials are also shown. (From Paper II).
hydrated due to contact with humid air (Fig. 6.1). The potassium is intercalated in between the MoS$_2$ sheets together with water (after air exposure) which leads to an expansion of the c lattice parameter (Table 6.2) [79, 109, 110]. Even if MoS$_2$ intercalation compounds with cations and neutral compounds are common in literature, the preparation method is generally significantly different than in the present case [78, 111]. To the author’s knowledge, catalyst activity data with alkali-intercalated MoS$_2$ have never been presented previously (Paper II). Potassium is present as K$_2$SO$_4$, but can also stay well dispersed on the catalyst surface, invisible for XRD. Ni$_2$S$_3$ is also present since the MoS$_2$ phase cannot accommodate all the nickel added. Table 6.2 summarizes crystal lattice parameters and crystallite size calculated from XRD patterns for the promoted and non-promoted MoS$_2$ catalysts as well the corresponding layer stacking heights.

Table 6.2. Physical properties of the catalysts derived from the XRD measurements

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MoS$_2$</th>
<th>K-Ni-MoS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline phases present</td>
<td>MoS$_2$</td>
<td>MoS$_2$ K$_x$MoS$_2$(H$_2$O)$_y$</td>
</tr>
<tr>
<td>Hexagonal lattice parameters, a (Å)</td>
<td>3.16</td>
<td>3.16</td>
</tr>
<tr>
<td>Hexagonal lattice parameters, c (Å)</td>
<td>12.3</td>
<td>13.34</td>
</tr>
<tr>
<td>Layer distance (Å)$^{b,c}$</td>
<td>6.15 (0)</td>
<td>6.67 (0.52) 18.37</td>
</tr>
<tr>
<td>Crystallite size (Å)$^d$</td>
<td>76</td>
<td>61</td>
</tr>
<tr>
<td>Number of stacked layers$^e$</td>
<td>12</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$ Prior to air exposure we expect the phase composition to be K$_x$MoS$_2$.
$^b$ Calculated by dividing lattice parameter c by 2.
$^c$ Values in parenthesis are expansion compared to crystalline MoS$_2$.
$^d$ Calculated from the XRD measurements of the most intense phase peak (002) using the Scherrer equation.
$^e$ Calculated from crystallite size divided by layer distance.
Chapter 7

Reaction equipment and analytical system

In this chapter the equipment and procedures used in the high-pressure catalytic tests are presented, but to the greatest extent the chapter is devoted and focused on the work performed in the development of a rapid and accurate analytical system for analyzing HAS products (Paper I). Analysis principles of the developed method are briefly presented and the results displayed e.g. in terms of product separation and closure of carbon material balance over the reactor. For complete and more in-depth method description, the reader is directed to the original paper (Paper I).

7.1 High pressure alcohol synthesis reactor

Higher alcohol synthesis needs to be performed under pressurized conditions since the reaction otherwise would be limited by thermodynamics (see section 3.3). However, most often even higher pressures are applied to increase alcohol selectivity and reaction rates.

The catalytic CO hydrogenation reactions were performed in a high-pressure downdraft stainless-steel fixed-bed reactor (i.d. 9 mm) with 0.65 g K–Ni–MoS₂ catalyst (45–250 µm) diluted by 3 g SiC (average pellet size = 77 µm). Gas flows were regulated by calibrated mass-flow controllers and reactor pressure was recorded by a pressure transducer located prior to the reactor oven which controlled a pressure valve located after the reactor. The reactor tube was heated by means of a cascade temperature-controlled oven with a sliding thermocouple in the catalyst bed and another placed in the oven. The whole reactor oven is located
inside a hot box heated to 185 °C, so preheating of the inlet gases and the reaction products are kept at this temperature. To avoid condensation of the products leaving the reactor, transfer lines, gas sample injection valves, etc. to the GC:s were heated to 190 °C. Product analysis was performed on-line with two gas chromatographs (GC:s). A detailed process and instrumentation diagram (PID) of the high pressure reaction apparatus and connections to the GC:s is shown in Fig. 7.1. However, the exact setup varied slightly and additional mass flow controllers (Papers III and VI) and a liquid gas separator (parts of Paper IV) were used in some of the experiments.

Fig. 7.1. Schematic overview of the gas feed, high-pressure reactor and analysis system connections. Main parts are from left to right: gas bottles, mass flow controllers, hot box preheating (and post heating), high temperature reactor, pressure controller, heated line 1, GC1, heated line 2 and sulfur GC. (From Paper I)
7.2 Development of an analytical system for higher alcohol synthesis products

The interest in syngas conversion to higher alcohols has motivated the development of improved analytical tools for product analysis, since the ones generally used suffer from a number of drawbacks and weaknesses (see Paper I).

Improved analytical tools for product analysis are very important since they can give more precise and accurate information from performed catalytic tests. This reduces uncertainty concerning the obtained results allowing more precise conclusions to be drawn. By identifying and quantifying more compounds more information can also be gained from the studies, to further improve the understanding of how MoS$_2$-based catalysts work, in the end hopefully permitting the development of better working MoS$_2$-based catalysts. Minor compounds may also be very important since they can give clues and information regarding product intermediates and formation pathways and how these are changed when the catalyst composition is changed.

An optimized HAS on-line gas chromatographic (GC) system and method were therefore developed (Paper I) to overcome the deficiencies in the methods used so far. The goal was to develop a system and method which are fast and simple to use, but especially with increased analytical accuracy and precision. The system should therefore be able to separate and quantify individual compounds, be totally automated, and the method good enough to achieve closing material balances over the catalytic reactor setup. The system was developed for the products formed over alkali-promoted MoS$_2$ catalysts for HAS, but is not limited to this catalyst type. Trace amounts of sulfur-containing compounds can also be found in the product when sulfur-containing catalysts are used and/or sulfur-containing syngas is fed. To understand to which degree this happens and in which form the sulfur is incorporated
into the liquid product, a system for light sulfur compound analysis was additionally developed.

The analytical system contains two GCs, where the first GC performs analysis of inorganic gases as well as hydrocarbons and oxygenates, making it possible to establish a full carbon material balance over the reactor, while the second GC is used for trace level analysis of sulfur compounds. All analysis was performed online using gas sampling valves and gas loops for sample introduction. To avoid condensation of products and achieve accurate measurements, all parts in contact with the sample (valves, sample loops, valve transfer lines) were located in an insulated valve oven heated to 190 °C, while transfer lines to and between the GC:s were kept to a minimum and held at the same temperature.

7.2.1 Analytical principles and product separation (GC1)

Analysis of the main products, all except sulfur, was carried out on-line using an Agilent 7890 gas chromatograph (GC 1 in Fig. 7.1) equipped with a thermal conductivity detector (TCD) and two flame ionization detectors (FID). A schematic overview of the main parts of the system is shown in Fig. 7.2.
Fig. 7.2. Schematic overview of GC1 (Agilent 7890). (From Paper I)

H₂, N₂, CO, CO₂ and methane were well separated and analyzed using three packed columns and a TCD (Fig. 7.2 upper part), while a two-dimensional (heart-cut) system with Deans switch and two capillary columns was responsible for analysis of organic compounds (alcohols, esters, hydrocarbons etc.) on the FIDs (Fig. 7.2 lower part). A very polar primary column (HP-FFAP) was chosen in order to separate light hydrocarbons (fast eluting) from oxygenates (later eluting) and separate individual oxygenates from each other. For the second dimension a capillary plot column (HP-Al₂O₃/S) suitable for light hydrocarbon analysis was selected. The Deans switch made it possible to direct the compounds eluting from the primary column, either through the secondary column to the secondary FID (FID B) or through an
inert restrictor column to the primary FID (FID A), depending on the Deans switch position (Fig. 7.3a and b, respectively).

By keeping the “Deans switch valve” initially in the on position and later switch it to the off position (Fig. 7.3a-b), a very good separation between individual oxygenates and hydrocarbons could be achieved. Chromatograms of the compounds produced and identified in the first (hydrocarbons) and second dimension (oxygenates), respectively, are presented in Figs. 7.4-7.5.

![Diagram](image)

Fig. 7.3. (a and b) Flow path for helium (carrier) and sample compounds when the Deans switch valve is in “on” and “off” position, respectively (GC1, Agilent 7890). (From Paper I)
Fig. 7.4. Example chromatograms detected on the first FID detector (hydrocarbon channel). Reaction conditions: 340 °C, GHSV = 6000 ml/(g\text{cat}\cdot h), \text{H}_2/\text{CO} = 1. (From \textbf{Paper I})

1) Methane 8) t-2-Butene 15) 3-Methyl-1-butene 22) 2,3-Dimethylbutane 29) 1-Hexene
2) Ethane 9) 1-Butene 16) t-2-Pentene 23) 2-Methylpentane 30) c-2-Hexene
3) Ethene 10) Isobutene 17) 2-Methyl-2-butene 24) 3-Methyl pentane 31) 2,4-Dimethylpentane
4) Propane 11) c-2-Butene 18) 1-Pentene 25) n-Hexane 32) 2,3-Dimethylpentane
5) Propene 12) Isopentane 19) 2-Methyl-1-butene 26) t-4-Methyl-1-2-pentene 33) 2-Methylhexane
6) Isobutane 13) n-Pentane 20) c-2-Pentene 27) Various hexene isomers 34) 3-Methylhexane
7) n-Butane 14) Cyclopentene 21) 2,2-Dimethylbutane 28) 2-Methyl-1-pentene 35) Heptane
Fig. 7.5. Example chromatograms detected on the second FID detector (oxygenate channel). Reaction conditions: 340 °C, GHSV = 6000 ml/(g_{cat} h), H_2/CO = 1. (From Paper I)

1) Acetaldehyde 10) 2-Butanone 20) 2-butanol 30) i-Pentyl propionate
2) Methyl formate 11) Methyl propanoate 21) Butyl formate 31) 3- and 2-methyl-1-Butanol
3) Propanal 12) 2-propanol 22) 1-Propanol 32) Penta propionate
4) i-Butanal 13) Ethanol 23) Propyl propionate 33) 1-Pentanol
5) Acetone 14) Ethyl propionate 24) n-Butyl acetate 34) 2-Methylpentanol
6) Methyl acetate/ 15) Ethyl isobutanoate 25) i-Butyl propionate 35) 2-Ethyl-1-butanol
Ethyl formate 16) Propyl acetate 26) i-Butanol/Isobutyl isobutanoate 36) 4-Methylpentanol
7) Butanal 17) 3- and 2-Pentanone 27) 2-Pentanol 37) 3-Methylpentanol
8) Ethyl acetate 18) Methyl butanoate 28) Butyl propionate/3-Methylbutyl acetate 38) 1-Hexanol
9) MeOH 19) i-Butyl acetate 29) 1-Butanol/Propyl butanoate
7.2.2 Material balance, selectivity, conversion and calibration (GC1)

CO conversion and product selectivity were ascertained from the TCD measurements using a premixed syngas containing 4% N\textsubscript{2} internal standard. With the internal standard method CO, H\textsubscript{2}, CO\textsubscript{2} and CH\textsubscript{4} molar flow rates (\(F\)) are decided by the measured compound TCD area (\(A\)) and the compound response factor (\(K\)) relative the internal standard. The compounds’ response factors relative internal standard (\(K_{i/N_2}\)) were found by calibration with two certificated gases standards, each containing CO, H\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} with known composition. The definitions and calculations of CO conversion (\(X_{CO}\)) and methane selectivity (\(S_{CH_4}\)) from TCD measurements are shown in Eqs. 7.1 - 7.3. Selectivity is expressed in carbon% on a CO\textsubscript{2}-free basis (and is so throughout this thesis unless explicitly stated).

\[
X_{CO} = \frac{F_{CO}^{in} - F_{CO}^{out}}{F_{CO}^{in}} = 1 - \frac{A_{CO}^{out}/A_{CO}^{in}}{A_{N_2}^{out}/A_{N_2}^{in}} \quad \text{CO conversion} \quad (7.1)
\]

\[
S_{CH_4} (CO_2\text{-free}) = \frac{F_{CH_4}}{F_{org.}} \quad \text{Methane selectivity} \quad (7.2)
\]

\[
S_{CH_4, TCD} = \frac{F_{CH_4}}{F_{CO}^{in} - F_{CO}^{out} - F_{CO_2}} = \frac{A_{CH_4}/A_{N_2}^{out}}{K_{CH_4/N_2}} \left( \frac{A_{CO}^{in}/A_{N_2}^{in} - A_{CO}^{out}/A_{N_2}^{out}}{K_{CO/N_2} - A_{CO}/A_{N_2}^{out} / K_{CO_2/N_2}} \right) \quad (7.3)
\]

Methane selectivity on the TCD detector

The internal normalization method was used for determining the selectivity to organic compounds since all injected material is
eventually detected on the FIDs. Eq. 7.4 shows this for determining methane selectivity, while other selectivities are determined in an equivalent way.

\[ S_{CH_4,FID}^{(CO_2\text{-free})} = \frac{n_{CH_4}}{n_{\text{org.}}} = \frac{A_{CH_4} \cdot R_{CH_4}}{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (A_{ij} \cdot R_{ij})} \]  

Selectivity is calculated from the measured FID area \( (A) \) of the compound of interest (methane in Eq. 7.4) and its corresponding FID response factor \( (R) \) (due to non-unity response of the carbon atoms attached to oxygen) divided by the areas of all organic carbon molecules \( (A_{ij}) \) (alcohols, hydrocarbons, esters etc. of different carbon lengths) with corrected responses \( (R_{ij}) \) summed together (Eq. 7.4).

The response factor difference between oxygenates and hydrocarbons are large and therefore significant errors occur if unity is used also for oxygenates. FID relative response factors (carbon response per carbon in alcohol relative carbon in hydrocarbon) for the three shortest alcohols determined by calibration are as follows: \( \text{RRF}_{\text{Methanol}} = 0.70 \), \( \text{RRF}_{\text{Ethanol}} = 0.73 \) and \( \text{RRF}_{1\text{-Propanol}} = 0.83 \).

As seen the methane selectivity can therefore be decided from the TCD and FID measurements independently of each other, meaning that they should ideally be equal to each other. Methane also creates a link between the two different types of detectors and makes a complete carbon material balance \( (MB) \) over the reactor possible (Eq. 7.5),
where $F_{C\text{ out}}$ and $F_{C\text{ in}}$ are total carbon flows into and out from the reactor, respectively. The carbon flow of organic molecules ($F_{C\text{ org}}$) is calculated from the definition of methane selectivity (Eq. 7.2). Eq. 7.5 therefore is equal to 100% when the carbon flow into the reactor is equal to the carbon flow out of the reactor, meaning that the measurement method works and a complete material balance is achieved.

### 7.2.3 Method validation and conclusions (GC1)

The performance of the analytical system was tested during a period of 80 h using the reactor system loaded with a K-Ni-MoS$_2$ catalyst and a syngas feed with a $H_2/CO$ ratio=1. The gas hourly space velocity (GHSV) and temperature was varied in order to achieve very different product selectivities and CO conversions. In this way it was possible to validate that the analytical method works well, independently of product composition and CO conversion level.

The methane selectivity determined from both detector types (TCD and FID) changed in a coherent way and the difference between them was always very small (Fig. 7.6), independently of CO conversion and product composition (Table 7.1). This is in addition to a carbon material balance of around 99.5% (Fig. 7.6) over the reactor ($C_{\text{ in}}/C_{\text{ out}}$), regardless of the product composition, shows that the method works well under the studied circumstances. The use of internal standard for the TCD measurements and careful calibration of the FID response factors for alcohols (which are far from unity) are believed to be among
the important factors for the success. Since the material balance does not show any signs of failing in the wide test range studied (in terms of product composition and CO conversion) the method is believed to work well also at significantly higher or lower conversion levels and with other HAS catalysts giving different product compositions.

To conclude, a totally online method was developed which is simple and fast to use. Virtually all compounds are individually separated and quantified. The closing material balance under all and very different product composition displays that the method works well and the quantification is trustworthy.

Table 7.1. Important reaction products for a few reaction conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>370</th>
<th>340</th>
<th>340</th>
<th>340</th>
<th>340</th>
<th>340</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-conversion (%)</td>
<td>31.4</td>
<td>17.8</td>
<td>8.4</td>
<td>5.8</td>
<td>4.1</td>
<td>3.4</td>
</tr>
<tr>
<td>GHSV (ml/(gcat h))</td>
<td>2750</td>
<td>2750</td>
<td>6000</td>
<td>9230</td>
<td>13,845</td>
<td>18,510</td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>57.2</td>
<td>74.0</td>
<td>81.3</td>
<td>84.3</td>
<td>86.5</td>
<td>87.8</td>
</tr>
<tr>
<td>EtOH</td>
<td>10.6</td>
<td>25.7</td>
<td>43.0</td>
<td>50.1</td>
<td>55.7</td>
<td>59.5</td>
</tr>
<tr>
<td>1-PrOH</td>
<td>23.2</td>
<td>38.1</td>
<td>32.9</td>
<td>29.7</td>
<td>26.7</td>
<td>24.6</td>
</tr>
<tr>
<td>1-BuOH</td>
<td>15.3</td>
<td>8.0</td>
<td>4.2</td>
<td>3.5</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>2.5</td>
<td>0.6</td>
<td>0.28</td>
<td>0.21</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>Hydrocarbons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>34.2</td>
<td>18.2</td>
<td>12.9</td>
<td>10.0</td>
<td>8.5</td>
<td>7.6</td>
</tr>
<tr>
<td>Ethane</td>
<td>25.9</td>
<td>15.4</td>
<td>10.7</td>
<td>8.3</td>
<td>6.8</td>
<td>5.9</td>
</tr>
<tr>
<td><strong>Aldehydes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>3.3</td>
<td>1.2</td>
<td>0.78</td>
<td>0.50</td>
<td>0.42</td>
<td>0.37</td>
</tr>
<tr>
<td><strong>Esters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl acetate/methyl formate</td>
<td>4.3</td>
<td>5.7</td>
<td>4.0</td>
<td>4.1</td>
<td>3.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.8</td>
<td>2.3</td>
<td>2.3</td>
<td>2.7</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Methyl propionate</td>
<td>1.1</td>
<td>1.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Ethyl propionate</td>
<td>0.4</td>
<td>0.55</td>
<td>0.29</td>
<td>0.27</td>
<td>0.21</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>Ketones</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.37</td>
<td>0.12</td>
<td>0.07</td>
<td>0.04</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.17</td>
<td>0.12</td>
<td>0.13</td>
<td>0.13</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>1.0</td>
<td>0.25</td>
<td>0.29</td>
<td>0.15</td>
<td>0.05</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 7.6. CO conversion, methane selectivity (calculated from TCD and the two FID measurements, respectively) as well as carbon balance over the reactor (C$_{in}$/C$_{out}$) for indicated reaction conditions. For methane selectivity based on the TCD and FID measurements, only positive and negative uncertainty bars, respectively, are presented to make the figure clearer. Constant reaction conditions: pressure = 91 bar and syngas molar ratio H$_2$/CO = 1. (From Paper I)
7.2.4 Trace sulfur analysis (sulfur GC)

For trace level analysis of sulfur products formed with MoS$_2$-based catalysts and/or sulfur-containing feed gas, an on-line Agilent 6890 GC equipped with an Agilent dual plasma 355 sulfur chemiluminescence detector (SCD) was used and a method developed. It is an extremely sensitive and selective sulfur detector which provides a linear and equimolar response to sulfur compounds without interference from most sample matrices ($10^7 < \text{g S/g C}$) [112, 113]. It is therefore a powerful detector and useful when trace sulfur compounds are to be measured in complex hydrocarbon/alcohol HAS product. The sulfur reactions taking place in the dual plasma burner (Eq. 7.6) and SCD (Eq. 7.7) are shown below together with the light emitted and used for quantification [113].

\[
\text{S-compound} + \text{O}_2 + \text{H}_2 \rightarrow \text{SO} + \text{other products} \quad (7.6) \\
\text{SO} + \text{O}_3 \rightarrow \text{SO}_2^* \rightarrow \text{SO}_2 + \text{hv} (300–400 \text{ nm}) \quad (7.7)
\]

All parts in contact with the sample were chosen for sulfur inertness together with a column suitable for light sulfur compounds analysis at trace level (GS-GasPro 30m x 0.32mm). In this way it was possible to perform separation of COS from H$_2$S and other light sulfur gases without the use of sub-ambient temperature. Calibration down to 5 ppm sulfur was performed and major sulfur components identified by retention time matching and/or MS fragmentation patterns. This system makes it possible to measure trace amounts of sulfur online simply and quickly, while the sulfur compounds can be identified and quantified. It is thus possible to follow and understand what affects sulfur incorporation, depending on reaction conditions or sulfur addition in the feed gas, as is described in Paper III and presented in chapter 9 of this thesis.
Chapter 8

Effect of operation conditions and gas feed composition on product distribution

This chapter summarizes the results from Papers II-III, for more details and in-depth discussion the reader is referred to these publications.

In Paper II the focus was to study the effect of the operating conditions space velocity and temperature on product distribution, since e.g. secondary reactions of previously produced reaction products seem to be of great importance for selectivity and activity in CO hydrogenation over MoS$_2$-based catalysts. To obtain clues about how these reactions occur and are linked, correlation patterns between the various products (alcohols, olefins, paraffins, esters, aldehydes, etc.) and how they are affected by the process parameters were studied. A potassium and nickel-promoted MoS$_2$ catalyst for alcohol synthesis was mainly evaluated, but for comparison a non-promoted MoS$_2$ catalyst was additionally tested.

In Paper III the main focus was to study the effect of CO$_2$-containing syngas, relative CO$_2$-free syngas under identical reaction conditions and identical inlet H$_2$ and CO partial pressures. The effect of increased partial pressures of H$_2$ and CO was also studied, and to some extent also the effect of changed gas hourly space velocity (GHSV). A K-Ni-MoS$_2$ catalyst was used and the study was performed during 360 h on stream.
8.1 Effect of temperature and space velocity on CO conversion and water-gas shift

In Paper II the operation conditions gas hourly space velocity (GHSV) and temperatures were varied over a fairly wide range while major and minor products were carefully monitored and quantified using the analytical system presented earlier (Paper I).

In Fig. 8.1 the CO conversion for the K-Ni-MoS₂ catalyst is shown when operation conditions were varied. In addition the CO conversion for the non-promoted MoS₂ catalyst at 370 °C is displayed. The product composition reveals that the water-gas shift reaction is very close to equilibrium under all conditions with the K-Ni-MoS₂ catalyst, while it is fairly far from it with the MoS₂ catalyst at low temperature and high space velocity conditions.

![Graph showing CO conversion at specified gas hourly space velocities (GHSV) and temperatures for K-Ni-MoS₂ and MoS₂ catalysts. Experimental conditions: H₂/CO=1, P=91 bar. (From Paper II)]
8.2 Selectivity for the promoted catalyst (K-Ni-MoS\(_2\))

Regardless of whether CO conversion was increased or decreased by changed space velocity or varied temperature, a clear trend in alcohol and hydrocarbon selectivity can be witnessed with the K-Ni-MoS\(_2\) catalyst (Fig. 8.2). As the CO conversion increased the alcohol selectivity decreased while the hydrocarbon selectivity increased. Non-alcohol oxygenates were also produced in smaller amounts over this catalyst (Fig. 8.2). This group mainly consists of short aldehydes (largely acetaldehyde) and esters (e.g. ethyl acetate) together with very small amounts of ketones (e.g. acetone).

![Fig. 8.2. Oxygenates, alcohols and hydrocarbons selectivity (CO\(_2\)-free) at different conversion levels over K-Ni-MoS\(_2\). Temperature levels were 330, 340, 350, 370 °C and for each temperature the space velocity 2400, 6000, 12000 and 18000 ml/(g\(_{\text{cat}}\) h) was varied. Fixed experimental conditions: H\(_2\)/CO=1, P=91 bar. (From Paper II)
Increased conversion not only led to lower alcohol selectivity, the alcohol distribution also switched towards longer alcohols. At low conversion level (i.e high space velocity and low temperature), the selectivity to methanol is high and a small amount of methane is produced (Fig. 8.3). This indicates that methanol is a primary product. As the conversion is increased (by decreased space velocity and/or increased temperature) selectivity gradually shifts towards longer and longer alcohols (Figs. 8.4-8.6) which are thermodynamically more stable than the shorter ones, but also towards methane and other hydrocarbons which are more stable than alcohols (Figs. 8.3, 8.7-8.8). Alcohols appear to participate in various secondary reactions in which they grow into longer alcohols or are hydrogenated and dehydrated to hydrocarbons. The common formation pathways for longer alcohols and hydrocarbons (involving secondary reactions), consequently makes it inherently difficult to achieve both high syngas conversion and high alcohol selectivity over this catalyst type.

Alkali-promoted MoS$_2$ catalysts have been found to mainly produce linear alcohols [67, 114] therefore the high isobutanol (and also branched pentanols) selectivity, especially pronounced at high temperature (370 °C) and low space velocity, (2400 ml/(g$_{\text{cat}}$ h)) was unexpected (Fig. 8.5). The higher reaction temperature and higher CO conversion level than in most studies, might partly explain this fact, but the knowledge about branched alcohol formation can in general be described as absent. Interesting to notice is also that the high propene selectivity coincided with the high level of i-BuOH selectivity (compare Fig. 8.5 and Fig. 8.8). Possibly, CO insertion into an adsorbed propene-like species followed by hydrogenation is responsible for i-BuOH formation. It can be speculated that ethene and other olefins can grow to longer alcohols in an equivalent way.
Fig. 8.3. Methane and methanol selectivities (CO$_2$-free) at different conversion levels over K-Ni-MoS$_2$. Reaction conditions as in Fig. 8.2. (From Paper II)

Fig. 8.4. Ethanol and propanol selectivities (CO$_2$-free) at different conversion levels. Reaction conditions as in Fig. 8.2. (From Paper II)
Fig. 8.5. Isobutanol and branched pentanol selectivities (CO$_2$-free) at different conversion levels over K-Ni-MoS$_2$. Reaction conditions as in Fig. 8.2. (From Paper II)

Fig. 8.6. n-Butanol and n-pentanol selectivities (CO$_2$-free) at different conversion levels. Reaction conditions as in Fig. 8.2. (From Paper II)
Fig. 8.7. Ethane and ethene selectivities (CO$_2$-free) at different conversion levels over K-Ni-MoS$_2$. Reaction conditions as in Fig. 8.2. (From Paper II)

Fig. 8.8. Propane and propene selectivities (CO$_2$-free) at different conversion levels. Reaction conditions as in Fig. 8.2. (From Paper II)
The effect of temperature and space velocity on space time yields for hydrocarbons and alcohols are presented in Fig. 8.9. Space time yield (STY) to alcohols decreases with decreased space velocity mainly due to greatly reduced methanol and ethanol STYs, while branched alcohol STY and hydrocarbon STY increase. The increased STYs for branched alcohols and hydrocarbons with reduced space velocity indicate that they are produced by secondary reactions.

![Graph showing yields of alcohols and hydrocarbons at specified space velocities and temperatures over the K-Ni-MoS₂ catalyst. Fixed experimental conditions: H₂/CO=1, P=91 bar. (From Paper II)](image)

8.3 Selectivity for the non-promoted catalyst (MoS₂)

Predominantly paraffins are produced over the non-promoted MoS₂ catalyst, but also minor amounts of olefins and alcohols. This highlights the role of alkali, altering the distribution from paraffins to alcohol (oxygenates) and olefins. Selectivities for alcohol and paraffins under two tested conditions can be seen in the ASF-plot.
(Fig. 8.10). For a catalyst generally found to produce methane (methanation catalyst), the elevated pressure applied appears to be the main reason for the high selectivity to longer hydrocarbons in this study [115]. Product distribution is to a relatively low extent affected by space velocity changes, while temperature influences the product distribution to a significantly larger degree. The alcohol selectivity varied between 0.5-4.5% while the olefin selectivity stayed within 0.2-1% under the conditions studied (1830-18200 ml/(g\text{cat} h), 340-370 °C).

That the alcohol and olefin selectivities for the non-promoted MoS\text{2} are decreased by decreased space velocity or increased temperature indicates that the alcohols and olefins may be consumed in secondary reactions and hydrogenated to paraffins.

![Graph](https://via.placeholder.com/150)

Fig. 8.10. ASF plot for normal paraffins and alcohols for the MoS\text{2} catalyst. Values next to the respective carbon number display selectivity (S\text{n}) in carbon% (CO\text{2}-free). CO conv. (370 °C)=15.8 %, CO conv. (340 °C)=11.3 %. Experimental conditions: H\text{2}/CO=1, GHSV=6000 ml/g\text{cat}/h, P=91 bar. (From Paper II)
In the C₃-C₆ range the paraffins were distributed in accordance with the ASF distribution (linear correlation in the ASF plot) and so were also the C₁-C₃ alcohols, showing similar chain growth probabilities, while deviations were found for C₁ and C₂ paraffins (Fig. 8.10).

### 8.4 Alkali effect

Promoting the catalyst with alkali not only creates a great change in the alcohol-to-hydrocarbon ratio, it also changes the olefin-to-paraffin ratio profoundly. While paraffins are totally dominating over the non-promoted catalyst (>99%), olefins are under most circumstances in majority with the promoted catalyst (Figs. 8.7-8.8). It seems that one of the effects of potassium addition is greatly reduced catalyst hydrogenation ability, in line with the effect of alkali in CO hydrogenation over transition metal catalysts [116-118] and the reduced ethylene hydrogenation over a Co-MoS₂ catalyst [119]. Reduced hydrogenation activity might be a necessary key step in achieving alcohol formation, since the alcohol (or alcohol precursor) otherwise quickly would be hydrogenated (and dehydrated) to the corresponding hydrocarbon.

### 8.5 Correlation between alcohol, aldehyde and olefin selectivities

The developed product analysis method made it possible to follow the product distributions for all important product groups such as aldehydes, olefins, esters, paraffins and alcohols in a very detailed way, therefore making it possible to obtain information about the correlation between different product groups with the hope of providing clues about the product formation mechanism.
Aldehyde and alcohol selectivities for identical carbon skeletons, for both branched and non-branched products under all sixteen tested conditions (four different temperatures and four different space velocities) are all strongly correlated. A few of these conditions are illustrated in the ASF distribution plots (Fig. 8.11a-e). The fact that the n-aldehyde and n-alcohol plots are copies of each other (with a y-axis offset), displaying identical deviations and chain growth probabilities, clearly indicates that they share a common intermediate. The termination probabilities to aldehyde and alcohol, respectively, from this common C<sub>x</sub> intermediate, are very different reflecting their very different product selectivities, but the ratio between aldehyde and alcohol termination probability is independent of chain length as seen by the identical shape of the ASF plots. The termination probability ratio between aldehyde and alcohol spans between 6% at the highest tested temperature (370°C) and 3.5% at the lowest tested temperature (330°C). The alcohol is possibly formed by hydrogenation of the thermodynamically less stable aldehyde-like surface species. Also olefin selectivities appear to be correlated to alcohol (and aldehyde) selectivities (Fig. 8.11a-e), which is especially clear in Fig. 8.11a when the catalyst surface most probably gets depleted in C<sub>2</sub> species (due to low conversion rate from C<sub>1</sub> to C<sub>2</sub> species and fast conversion of C<sub>2</sub> to C<sub>2+</sub> species) under the high temperature and low space velocity conditions. This points towards it being formed from the same intermediate as aldehydes and alcohols, but the correlation is not as strong as between the alcohols and aldehydes. Compared to the distribution witnessed for n-alcohols, especially ethene deviates by being formed to a lower degree than expected at low temperature and high space velocity, while being produced in higher concentration than expected at high temperature and low space velocity (Fig. 8.11a-e). Higher temperature and lower space velocity might favor dehydration of ethanol (ethanol-like intermediate) to the thermodynamically more stable ethene (ethene-like intermediate). Some of this ethene
Fig. 8.11. ASF plots for n-alcohols, α-olefins, linear aldehydes and paraffins over K-Ni-MoS$_2$. Fixed experimental conditions: H$_2$/CO=1, P=91 bar.

a) GHSV= 2400 ml/(g$_{cat}$ h) and 370°C,
b) GHSV= 6000 ml/(g$_{cat}$ h) and 370°C,
c) GHSV=12000 ml/(g$_{cat}$ h) and 370°C,
d) GHSV=18000 ml/(g$_{cat}$ h) and 370°C,
e) GHSV=18000 ml/(g$_{cat}$ h) and 330°C.
(From Paper II)
is most probably also hydrogenated to ethane, favored by high temperature and low space velocity, even though the potassium promoter slows down the hydrogenation rate significantly.

By adding up the major linear reaction products for each carbon number (n-alcohol, n-paraffins and \(\alpha\)-olefins), a more linear ASF plot is created (more ASF-distributed product) compared to the plots for the individual product groups. This indicates that a common intermediate is responsible for both alcohol and hydrocarbon formation and that the chain growth probability is fairly constant and independent of chain length.

8.6 Alcohol chain growth

Alcohol synthesis catalysts based on MoS\(_2\) are chiefly described as producing linear alcohols, and the emphasis in the discussion on chain growth is around CO insertion into an alkyl group, where the alkyl is derived from an alcohol-like intermediate [69]. This chain growth mechanism fits well with the experimentally observed carbon chain length-dependent selectivities resembling the ASF distribution, since it is based on a chain growth step with a single carbon element (C\(_1\) monomer). The ASF distribution is followed quite well also in the present study, especially under low temperature and high space velocity conditions (e.g. Fig. 8.11e), indicating a mechanism similar to the one just described. However, as the temperature is increased and the space velocity decreased (CO conversion increased) branched alcohols start to be produced in substantial amounts (Fig. 8.5). The alcohol formation model therefore is incomplete and needs to be revised to deal also with branched alcohols. At higher CO conversion levels, branched alcohols even dominate over their linear counterpart (Figs. 8.5-8.6) (seen by comparing branched and straight C\(_4\) and C\(_5\) alcohols, respectively).
My interpretation is that alcohol chain growth could be thought of as a combination of two main reaction paths, linear growth and branched growth. In linear growth, the single carbon element is inserted into the carbon chain end (the first carbon) adsorbed onto the catalyst surface, therefore leading to straight-chain products. At low temperature it seems to dominate since the alcohol product contains mostly linear ASF-distributed alcohols, but as the temperature is increased and space velocity lowered, branched growth gains ground. In branched growth the carbon element is instead inserted on the “second carbon” of the carbon chain (and in close proximity to adsorption point), thus explaining the formation of branched products. According to this theory, linear growth and branched growth could reflect two quite different alcohol formation mechanisms or just be a small modification of the kinetics for a single formation mechanism. The two mechanisms could, for example, be CO insertion into an alkyl (derived from an alcohol-like intermediate) and aldol condensation (e.g. aldol condensation between C₃+C₁ species leading to the formation of isobutanol). An example of a single chain growth mechanism could be that an α-olefin-like species is involved and that the changed iso-butanol/n-butanol ratio with temperature simply could reflect the fact that isobutanol formation from propene at low temperature is kinetically limited and n-butanol formation favored, but as the temperature increases the thermodynamically more stable product, isobutanol, gains ground.

Santiesteban et al. hypothesized that propanol was produced from an ethene-like intermediate, based on the propanol isotope distribution when labeled MeOH was co-fed over a K-Co-MoS₂ catalyst [69].
8.7 Ester formation

Esters are together with aldehydes the main non-alcohol oxygenates over the promoted MoS$_2$ catalysts (Fig. 8.12). By looking closer into ester and alcohol selectivities under different conditions, it becomes clear that they are strongly correlated (Fig. 8.14a-d). The correlation is such that an ester can be thought of as being formed by two alcohol chains (with some hydrogen removed) (Fig. 8.13). E.g. the selectivity to propyl acetate (C$_3$+C$_2$) is correlated to the propanol (C$_3$) and ethanol (C$_2$) selectivities. The correlation between alcohol and esters also clearly indicates that esters are being formed by reactions between two alcohol precursor species.

![Graph showing ester and aldehyde selectivities at different conversion levels over the K-Ni-MoS$_2$ catalyst. Temperature levels were 330, 340, 350, 370 °C and for each temperature space velocity 2400, 6000, 12000 and 18000 ml/(g cat h). Fixed experimental conditions: H$_2$/CO=1, P=91 bar. (From Paper II)](image-url)

Fig. 8.12. Ester and aldehyde selectivities at different conversion levels over the K-Ni-MoS$_2$ catalyst. Temperature levels were 330, 340, 350, 370 °C and for each temperature space velocity 2400, 6000, 12000 and 18000 ml/(g cat h). Fixed experimental conditions: H$_2$/CO=1, P=91 bar. (From Paper II)
Fig. 8.13. Parts of the ester, part 1 containing the carbonyl group (acyl or formyl group) and part 2 containing the alkoxy group.

The alkoxy part of the ester molecule (x-axis in Fig. 8.14a-d) is correlated to the alcohol selectivity in an almost proportional way, with the exception of methyl esters, which are being formed in higher quantities than predicted from the methanol selectivity. It can be speculated that this is due to an increased reactivity of the C₁ species (a methanol-like species, e.g. methoxy anion) compared to the corresponding longer-chained species.
Fig. 8.14. Correlation between ester and alcohol chain lengths at 370 °C for the K-Ni-MoS$_2$ catalyst. See next page for Fig. 8.14c-d and further information.
Fig. 8.14. Correlation between ester and alcohol chain lengths at 370 °C for the K-Ni-MoS$_2$ catalyst. Fixed experimental conditions: H$_2$/CO=1, P=91 bar. The ester selectivity (mol%) is multiplied 100 times for simpler comparison with the alcohol.
(a) space velocity 2400 ml/(g$_{\text{cat}}$ h), (b) space velocity 6000 ml/(g$_{\text{cat}}$ h), (c) space velocity 12000 ml/(g$_{\text{cat}}$ h) and (d) space velocity 18000 ml/(g$_{\text{cat}}$ h). (From Paper II)
The opposite correlation was found for the carbonyl part of the ester (y-axis in Fig. 8.14a-d), i.e. much less formate esters (C₁) are formed than expected, while the acetate (C₂) and propionate (C₃) esters are correlated almost proportionally to the corresponding ethanol (C₂) and propanol (C₃) alcohol selectivities.

Santiesteban et al. performed co-feed experiments with isotope-labeled methanol (¹³C) and showed that the methyl group of methyl acetate is enriched with ¹³C as well as the terminal carbon in the acetate part, while the carbonyl carbon consists of ¹²C derived from the syngas [69]. For methyl formate the terminal group was also ¹³C enriched, meaning it is methanol-derived while the carbonyl carbon lacks ¹³C meaning that it is derived from the syngas. These results are in line with the experimental findings of this study.

8.8 Effect of CO₂, H₂ and CO partial pressure

As presented earlier in this chapter, the product distribution is greatly affected by residence time and temperature in the reactor, however, it is uncertain to which extent reaction products such as CO₂ influence formation rates and product distribution. It is of great interest to understand the effect of CO₂ on formation rates, since the CO₂ pressure in the reactor increases as the syngas conversion increases, as it is a main reaction product. Another reason for studying CO₂-containing syngas is that raw syngas usually contains CO₂, and it may be of interest to understand the effect of CO₂-containing syngas being fed to the reactor. To clarify the effect of CO₂ on product selectivity and formation rates, a syngas feed containing CO₂ was compared with one free of CO₂, while the inlet H₂ and CO partial pressures and reaction conditions were kept identical (Paper III).
Fig. 8.15. Product selectivity (a) and space time yield (b) of specified organic products under conditions A and B. T=340 °C, P$_{tot}$=100 bar, GHSV=6920 ml/g$_{cat}$ h. Period A= 38.4% each of H$_2$ and CO, 3.2% N$_2$, 20% He. Period B$_1$= as period A but CO$_2$ is used instead of He. (Adapted from Paper II)
CO₂ in the feed was found to greatly alter selectivity towards increased methanol selectivity while the ethanol and longer alcohols (C₃+OH) selectivities decreased under the studied conditions (Fig. 8.15). Additionally, the presence of CO₂ profoundly reduced CO conversion and the formation of organic products, which, together with the reduced higher alcohol selectivity, meant greatly reduced higher alcohol yield (Fig. 8.15). The water-gas shift reaction was found to be close to equilibrium under all tests conditions (determined from material balance) meaning that large amounts of water were therefore produced when CO₂ was fed to the reactor. It made it impossible to discern whether CO₂ or water is responsible for the activity and selectivity changes. With CO₂ present in the feed, the reverse water-gas shift reaction takes place until the WGS equilibrium is reached (eq. 3.7), meaning that the H₂ partial pressure is reduced and the CO and H₂O partial pressures increased. A lower H₂/CO ratio normally would favor an increased alcohol and hydrocarbon chain growth (see next paragraph), but the opposite was witnessed with CO₂ in the feed. Thus CO₂ (H₂O) causes this effect. CO₂ (H₂O) is also responsible for the great reduction in product yield, since the H₂ and CO partial pressure changes (due to the WGS reaction) are fairly small, and should only influence the yield to a minor extent. Additionally, the negative effect on yield due to the reduced H₂ partial pressure, should to a great extent be compensated for by the increased CO partial pressure, giving a positive contribution to the amount of product (see next paragraph).

In a similar manner as with CO₂ addition, increased partial pressures of H₂ and CO were studied (Paper III). High H₂/CO ratio (H₂/CO=1.52) clearly favors total product yield, especially methanol yield, while low H₂/CO-ratio (H₂/CO=0.66) leads to lower total product yield due to lower methanol and hydrocarbon yield while the formation of longer alcohols i.e. ethanol, propanol etc. is significantly increased. Without stating exact levels, clearly a
syngas feed with fairly low H$_2$/CO ratio and low levels CO$_2$ is preferred for achieving maximum productivity to longer alcohols.
Chapter 9

Sulfur in the product and effect of H₂S-containing feed

In this chapter topics related to sulfur in higher alcohol synthesis using a K-Ni-MoS₂ catalyst are discussed. The aim was to investigate the sulfur products being formed, their concentrations and how they were affected when sulfur (H₂S) was present or not present in the feed. The effect on syngas conversion and selectivity in the presence of sulfur was simultaneously studied. For more details and in depth information and discussion the reader is directed to the appended original paper (Paper IV).

9.1 Background and introduction

The level of sulfur in raw synthesis gas (mainly H₂S and some COS) is decided by the raw material, its origin and used production method. In general significantly higher sulfur levels are found in syngas derived from coal (0.1-2 %) than from biomass (20-200 ppm), while the sulfur in natural gas-derived syngas in general is removed before the syngas generation (often several % before cleaning) to avoid catalyst deactivation [120, 121].

An often emphasized asset of the MoS₂-based catalysts in HAS is the resistance to sulfur poisoning (in contrast to the sensitive metal catalysts). This property has been suggested to enable reduction in syngas cleaning needs and costs related to it. However, the use of sulfur-containing feed and catalyst might also lead to incorporation of small amounts of light sulfur compounds into the alcohol product, as indicated by early research by Dow
Chemical and later confirmed by Christensen et al. [67, 122]. The knowledge regarding the severity of this issue is very scarce, but nevertheless very important since even trace amounts of sulfur might create a need for product cleanup if the level is too high for the intended product use. The sulfur level in gasoline is e.g. limited to 30 ppmw in United States and 10 ppmw in the European Union [60, 123], meaning that the accepted sulfur limit of the alcohol portion of the fuel most certainly will be in that region too.

There are many questions that remain unanswered regarding the sulfur compounds produced over alkali-MoS$_2$ catalysts and their concentrations. This is important for understanding whether cleaning procedures are necessary and if so how they can best be performed. It is also of great importance to understand the effect sulfur in the feed has on both alcohol and hydrocarbon productivities so they can be optimized.

### 9.2 Sulfur products in condensate and gas phase

Two types of experiments were performed using a K-Ni-MoS$_2$ catalyst which beforehand had been operated for 1000 h on stream in sulfur-free syngas.

In the first experimental part, condensation of product was performed using a Peltier-cooled liquid gas separator operated at 9°C and reaction pressure (91 bar). Sulfur free syngas feed was used, thus the sulfur present in the product derived from the catalyst. An example chromatogram of the sulfur compounds in the product condensate can be seen in Fig. 9.1. Product identification and quantification of the produced sulfur compounds was achieved by the GC method for trace sulfur analysis described in section 7.2.3 (Paper I). Applied reaction conditions and determined sulfur concentrations in both the condensate and the gas phase are shown in Table 9.1.
Fig. 9.1. Chromatogram of sulfur products in collected condensate. Analysis was performed on an Agilent 6890 with dual plasma sulfur chemiluminescence detector (SCD). Reaction conditions during collection as in Table 9.1. (From Paper IV)

It is interesting to notice that although the catalyst has been exposed to sulfur-free syngas for a long time, the total sulfur content in the condensate (67 ppmw) is well above the sulfur legislation for gasoline in both the US and the EU, 10 and 30 ppmw, respectively. The main sulfur products in the condensate were methanethiol, ethanethiol, dimethyl sulfide (DMS) and ethyl methyl sulfide (EMS). Very small amounts of propanethiol (PrSH) were in addition produced (0.2 ppmw), this is much less than expected considering the fairly high PrOH/MeOH (PrOH/EtOH) ratio relative the PrSH/MeSH (PrSH/EtSH) ratio (see more in Paper IV). A number of unidentified sulfur compounds (see marked peaks in Fig. 9.1), all in concentrations within 0.4-2.4 ppmw S, were in addition present in the fuel.
Table 9.1. Sulfur products measured in gas phase and in liquid phase, respectively. Feed composition and reaction conditions: 4% N₂, 48% H₂ and 48% CO, GHSV=6920 ml/(g_cat·h), T=370 °C, P_tot=91 bar. CO conversion and selectivity under these conditions were: CO conv.=16.7%, S_Alc.=69.9%, S_HC=20.9, S_others=9.2%

<table>
<thead>
<tr>
<th>Sulfur compound</th>
<th>Concentration in gas phase (ppmv)</th>
<th>Concentration in condensate (ppmw S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COS</td>
<td>3.1</td>
<td>0.5</td>
</tr>
<tr>
<td>H₂S</td>
<td>14.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>0.5</td>
<td>13.8</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td>0.3</td>
<td>10.6</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>0.7</td>
<td>21.3</td>
</tr>
<tr>
<td>Ethyl methyl sulfide</td>
<td>0.1</td>
<td>12.2</td>
</tr>
<tr>
<td>Unidentified sulfur compounds</td>
<td>0.01</td>
<td>7.9</td>
</tr>
<tr>
<td>Total sulfur level</td>
<td>19</td>
<td>67</td>
</tr>
</tbody>
</table>

Christensen et al. are the only ones that have touched the issue of sulfur in the liquid product over MoS₂-based HAS catalysts [122]. They found ethanethiol, 1-propanethiol and 2-methyl-1-propanol, together with indications of dimethyl sulfide (DMS) and various thiophenes in the condensate, suggesting that 2-methyl-1-propanol and thiophenes were among the unidentified sulfur products (Fig. 9.1.). Diethyl sulfide is also expected due to the high ethanethiol concentration and the link between thiol and thioether formation (see Paper IV). The sulfur compounds in the gas phase were mainly H₂S and COS together with very low levels of other sulfur compounds, the same found in the condensate (Fig. 9.1.). The major products identified (MeSH, EtSH, DMS and EMS) appear reasonable based on literature where MoS₂ catalysts and a feed consisting of syngas or alcohols together with H₂S has been studied [124-130]. However, the high concentration of thioethers (DMS, EMS) relative thiols (MeSH, EtSH) was unexpected, based on the fact that thiols are the totally dominating products in the above-described studies and Christensen’s alcohol synthesis study
[122]. However, as described below, this is related to the low \( \text{H}_2\text{S} \) concentration (14 ppmv) in this study, while the \( \text{H}_2\text{S} \) concentration was very much higher in the other studies. Research by Paskach et al. also supports this, since the ratio DMS/MeSH increased greatly when the \( \text{H}_2\text{S}/\text{MeOH} \) feed ratio was decreased in their study [129].

9.3 Effect of \( \text{H}_2\text{S} \) on sulfur products

In the second experimental part, the liquid-gas separator was removed and all products analyzed online, while the effect of 170 ppm \( \text{H}_2\text{S} \) in the feed was compared with sulfur-free conditions. Presence of \( \text{H}_2\text{S} \) in the feed greatly increased the concentration of all sulfur compounds compared to sulfur-free feeding conditions and most of the sulfur remained in the form of \( \text{H}_2\text{S} \) (Fig. 9.2). The organic sulfur concentration in the product gas (excluding COS and \( \text{H}_2\text{S} \)) stayed within 15-18 ppmv when 170 ppmv \( \text{H}_2\text{S} \) was feed, compared to 1.5-3.5 ppmv under \( \text{H}_2\text{S} \)-free conditions (Fig. 9.3), meaning a fivefold difference, roughly speaking. Together with COS, formations of thiols (methanethiol and ethanethiol) were especially favored by the presence of \( \text{H}_2\text{S} \). The thioether concentration was also favored by \( \text{H}_2\text{S} \), however, to a much lower extent, meaning that the thiol/thioether ratio increased greatly when \( \text{H}_2\text{S} \) was present in the feed gas. Apparently, \( \text{H}_2\text{S} \) in the feed greatly favors thiol formation. While methanethiol was the totally dominating organic sulfur product when \( \text{H}_2\text{S} \) was present in the feed, dimethyl sulfide most often was found in higher concentration under \( \text{H}_2\text{S} \)-free conditions. There are indications that the thioethers might be formed by secondary reactions from the corresponding thiols or alcohol and thiol (see more in Paper IV), while thiols are believed to be formed by reactions between \( \text{H}_2\text{S} \) and alcohol or \( \text{H}_2\text{S} \) and syngas. Obviously some transient effects can be seen in this study, related to adsorption of sulfur (Fig. 9.2). Compared to the differences
between using H$_2$S-containing or H$_2$S-free feed this uncertainty is however small and does not conceal the main conclusions.

Fig. 9.2. Sulfur products found in high concentration (a) and low concentration (b) in products gas vs. time on stream and specified reaction conditions when no condensation of product was performed. Feed composition: 39.8% CO, 39.8% H$_2$ and 20.4% N$_2$. During the H$_2$S feed part the H$_2$S concentration was 170 ppm while the N$_2$ concentration was decreased equally much. $P_{\text{tot}}$=9.1 MPa and GHSV=6670 ml/(g$_{\text{cat}}$ h). (From Paper IV).
9.4 Effect of H$_2$S on CO conversion and product selectivity

Fig. 9.3 shows the effect of CO conversion and selectivity at a number of temperatures when H$_2$S was present and not present in the syngas feed. The CO conversion increased when H$_2$S was present in the feed, but the most remarkable alteration was found in the selectivities, where hydrocarbon selectivity was greatly increased at the expense of alcohol selectivity (Fig. 9.3).

![Figure 9.3](image)

The hydrocarbon selectivity increased mainly due to increased methane formation, while the distribution within the alcohol group shifted towards longer alcohols i.e. the C$_2$+OH/methanol ratio increased. Comparing the yields, it became clear that most of the...
increased CO conversion with added H$_2$S was due to an increased conversion to methane (and CO$_2$ due to the water-gas shift reaction). H$_2$S in the feed therefore appears to counteract the effect of potassium addition, making the catalyst behave more like one free from alkali promoter i.e. showing increased CO conversion, hydrocarbon (methane) selectivity and paraffin/olefin ratio while the alcohol selectivity is reduced.
Chapter 10

Final discussion and conclusions

Catalytic conversion of syngas (H₂/CO) to higher alcohols over MoS₂-based catalysts is an interesting alternative way of producing C₁-C₅ alcohol fuels and chemicals. In this thesis a number of important issues in the field of higher alcohol synthesis (HAS) from syngas over MoS₂-based catalysts are addressed. The catalytic tests have been performed in a high pressure fixed catalytic reactor with in-house prepared primarily potassium promoted Ni-MoS₂ catalysts and a syngas feed with H₂/CO-ratio=1. The catalysts were prepared by co-precipitation of nickel and thiomolybdate, which after drying was decomposed in the presence of alkali promoter. Alkali-promoted MoS₂-based catalysts are among the most promising catalysts for higher alcohol synthesis e.g. due to their high selectivity to longer alcohols as well as for being well adapted to syngas with low H₂/CO-ratio, which is typical for raw syngas derived from biomass or coal.

The first part of the work presented is focused on the effect of process parameters on product distribution and the correlation between different compounds over a K-Ni-MoS₂ catalyst. The alcohol and hydrocarbon selectivities were found to be greatly dependent on the CO conversion level. Increased CO conversion by means of increased temperature or decreased space velocity, both affect the product distribution in the same way with decreased alcohol selectivity and increased hydrocarbon selectivity. However, increased CO conversion leads to greater long-to-short alcohol chain ratio. This indicates that shorter alcohols are building blocks for longer alcohols and alcohols can be converted to hydrocarbons by secondary reactions (especially methanol converted to
methane). As a result, it is inherently difficult to reach both high single-path conversion and high alcohol selectivity over this catalyst type. The strong correlation between aldehyde and alcohol selectivities (C₂-C₆), displayed by identical deviations and chain growth probabilities, indicate that they derive from the same intermediate. Besides this, olefin and alcohol selectivities are correlated, but the correlation is not as strong as between aldehydes and alcohols. Fairly high levels of esters were also found in the product (up to 7-8% C) and the carbon chain correlation between alcohol (aldehyde) and ester selectivities is strong, displaying that their formation paths are linked. The ester selectivity is correlated almost proportionally to the selectivity of the two corresponding alcohol selectivities, meaning that e.g. ethyl propionate (C₅) selectivity is correlated to a combination of ethanol (C₂) and propanol (C₃) selectivities. Much less (alkoxy) formate esters and more methyl esters are, however, formed than expected according to the methanol content relative to the other alcohols.

The much greater olefin to paraffin ratio over the promoted MoS₂ catalyst compared to the non-promoted one indicates that one function of the potassium promoter is to greatly reduce the hydrogenation function of the catalyst. I therefore believe that reduced hydrogenation activity is a key step in achieving high alcohol and olefin selectivities.

The existence of CO₂ in the feed greatly reduced the yield to organic products while product distribution switched towards short alcohols and hydrocarbons, i.e. methanol selectivity was greatly increased and selectivity to longer alcohols decreased at the same time as the methane selectivity was increased while longer hydrocarbon selectivity decreased. However, if it is really CO₂ or H₂O that causes this effect is difficult to say since they are linked through the water-gas shift (WGS) reaction, which is close to equilibrium under all reaction conditions. Changing the H₂/CO ratio of the syngas feed clearly shows that high H₂/CO ratio (H₂/CO=1.52) favors total product yield, especially methanol yield.
Low H\textsubscript{2}/CO ratio (H\textsubscript{2}/CO=0.66) on the other hand leads to lower total product yield due to lower methanol and hydrocarbon yields while the longer alcohol formation i.e. ethanol, propanol etc. is significantly increased. A low H\textsubscript{2}/CO ratio syngas with no or only small amounts of CO\textsubscript{2} is therefore preferred for maximizing the higher alcohol yield and minimizing hydrocarbon and methanol formation.

MoS\textsubscript{2}-based catalysts’ tolerance to sulfur has often been presented as one of their most favorable characteristics in HAS. The sulfur tolerance makes it possible to reduce syngas cleaning needs (sulfur removal) and costs. However, as shown in the thesis, using sulfur-containing feed and/or sulfur-containing catalyst might also lead to incorporation of traces of light sulfur compounds in the product liquid. Previously, the knowledge regarding sulfur compounds formed and their concentrations was very limited. After 1000 h on stream using a K-Ni-MoS\textsubscript{2} catalyst and sulfur-free syngas feed, the product condensate collected was found to contain 67 ppmw of sulfur. The main sulfur compounds found were methanethiol, ethanethiol, dimethyl sulfide and ethyl methyl sulfide. Comparing the organic sulfur concentrations in the product under sulfur-free and 170 ppmv (H\textsubscript{2}S) sulfur-containing feed syngas, respectively, the organic sulfur concentration is roughly five times higher when sulfur is present and especially the thiol concentration is increased. Most of the sulfur however, was still present as H\textsubscript{2}S or transformed to COS. This means that both with and without sulfur in the feed, the sulfur concentrations in the liquid product is higher than allowed in the EU and the US for use in gasoline, meaning some kind of cleaning/distillation etc. procedure is necessary before it can be used as blendstock in gasoline. H\textsubscript{2}S in the feed additionally affects catalyst activity and selectivity. This was mainly due to an increased methane formation rate (and CO\textsubscript{2}) when H\textsubscript{2}S was present in the feed, thus increasing CO conversion and lowering alcohol selectivity.
In order to achieve accurate and trustworthy results from the high pressure catalytic tests described here earlier, a fully automatic on-line gas chromatography method was developed. The greatest advantage with the developed method is an almost complete product separation capability between the formed products (even minor compounds) and a well-closing carbon material balance over the reactor. Two-dimensional gas chromatography (2D-GC) with Deans switch was applied, making it possible to achieve good separation between individual hydrocarbons (olefins, paraffins, branched, straight etc.) in the first dimension and individual oxygenates (alcohols, esters, aldehydes etc.) in the second dimension. The organic products were measured on two flame ionization detectors (FIDs) and inorganic gases and methane on a thermal conductivity detector (TCD). Product composition and syngas conversion level were varied over a wide range by changes in process parameters in order to verify method consistency. A constant carbon material balance of around 99.5% over the reactor ($C_{in}/C_{out}$) was observed and consistent methane selectivity determined from both the FIDs and the TCD. This shows that the method works well and the aims were accomplished, i.e. to develop an easy to use and fast procedure, but especially a method with increased accuracy, precision and resolution, allowing truthful and precise conclusions to be drawn from the catalyst tests.

Further, the power of the successfully developed and described “sulfur GC” method using an on-line gas chromatograph (GC) equipped with dual plasma sulfur chemiluminescence detector (SCD) was presented. It was used for measuring trace sulfur compounds formed in the HAS product described earlier and was achieved by using non-sulfur adsorbing materials for parts in contact with the sample (tubing, valves, columns etc.), a very suitable detector and optimized operation conditions, making it possible to measure and quantify light sulfur products at trace level.
in a hydrocarbon matrix in an easy, accurate and reliable way which is inherently difficult.
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Finally, I send a warm thanks to my family who deeply cares about me and provides me with love and support.
## Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>2-dimensional</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>ASF</td>
<td>Anderson-Schulz-Flory</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BuOH</td>
<td>Butanol</td>
</tr>
<tr>
<td>DMS</td>
<td>Dimethyl sulfide</td>
</tr>
<tr>
<td>E10</td>
<td>A blend of 10 percent ethanol and 90% by volume gasoline</td>
</tr>
<tr>
<td>E15</td>
<td>A blend of 15 percent ethanol and 85% by volume gasoline</td>
</tr>
<tr>
<td>E85</td>
<td>A blend of 85 percent ethanol and 15% by volume gasoline</td>
</tr>
<tr>
<td>EMS</td>
<td>Ethyl methyl sulfide</td>
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<tr>
<td>EOS</td>
<td>Equation of state</td>
</tr>
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<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>EtSH</td>
<td>Ethanethiol</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>FT</td>
<td>Fischer-Tropsch</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hourly space velocity</td>
</tr>
<tr>
<td>HAS</td>
<td>Higher alcohol synthesis</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>M15</td>
<td>A blend of 15 percent methanol and 85% by volume gasoline</td>
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<td>MeOH</td>
<td>Methanol</td>
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<td>MeSH</td>
<td>Methanethiol</td>
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<td>Mass spectrometer</td>
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<td>ppmv</td>
<td>Parts per million on volume basis</td>
</tr>
<tr>
<td>RRF</td>
<td>Relative response factor</td>
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SCD  Sulfur chemiluminescence detector
SRK  Soave-Redlich-Kwong (equation of state)
STY  Space time yield
TCD  Thermal conductivity detector
XRD  X-ray diffraction
WGS  Water-gas shift
References


