

**HYDRODEOXYGENATION OF ALIPHATIC AND
AROMATIC OXYGENATES ON SULPHIDED CATALYSTS
FOR PRODUCTION OF SECOND GENERATION BIOFUELS**

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Abstract

Environmental concerns and diminishing petroleum reserves have increased the importance of biofuels for traffic fuel applications. Second generation biofuels produced from wood, vegetable oils and animal fats have been considered promising for delivering biofuels in large amount with low production cost. The abundance of oxygen in the form of various aliphatic and aromatic oxygenates decreases the quality of biofuels, however, and therefore the oxygen content of biofuels must be reduced. Upgrading of biofuels can be achieved by hydrodeoxygenation (HDO), which is similar to hydrodesulphurisation in oil refining. In HDO, oxygen-containing compounds are converted to hydrocarbons by eliminating oxygen in the form of water in the presence of hydrogen and a sulphided catalyst. Due to the low sulphur content of biofuels, a sulphiding agent is typically added to the HDO feed to maintain activity and stability of the catalyst.

The aim of this work was to investigate HDO using aliphatic and aromatic oxygenates as model compounds on sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts. The effects of side product, water, and of sulphiding agents, H₂S and CS₂, on HDO were determined. The primary focus was on the HDO of aliphatic oxygenates, because a reasonable amount of data regarding the HDO of aromatic oxygenates already exists.

The HDO of aliphatic esters produced hydrocarbons from intermediate alcohol, carboxylic acid, aldehyde and ether compounds. A few sulphur-containing compounds were also detected in trace amounts, and their formation caused desulphurisation of the catalysts. Hydrogenation reactions and acid-catalysed reactions (dehydration, hydrolysis, esterification, E₂ elimination and S_N2 nucleophilic substitution) played a major role in the HDO of aliphatic oxygenates. The NiMo catalyst showed a higher activity for HDO and hydrogenation reactions than the CoMo catalyst, but both catalysts became deactivated

because of desulphurisation and coking. Water inhibited the HDO, but the addition of H₂S effectively eliminated the inhibition. The addition of H₂S enhanced HDO and stabilised the selectivities but did not prevent deactivation of the catalysts. The effect of H₂S was explained in terms of promotion of the acid-catalysed reactions due to enhanced catalyst acidity. Water and the sulphiding agents added to the HDO feed suppressed hydrogenation reactions on the NiMo catalyst but did not affect them on the CoMo catalyst. The addition of H₂S resulted in less hydrogen consumption and coke formation than the addition of CS₂, but the product distribution was shifted such that the carbon efficiency decreased. It was concluded that, for the HDO of aliphatic oxygenates, H₂S was superior to CS₂ as a sulphiding agent.

The HDO of phenol, used as a model aromatic oxygenate, produced aromatic and alicyclic hydrocarbons in parallel routes in which the primary reactions were direct hydrogenolysis and hydrogenation, respectively. The addition of H₂S on both catalysts inhibited the HDO due to competitive adsorption of phenol and H₂S, and affected the hydrogenation reactions in the same way as in the HDO of aliphatic oxygenates. The opposite effects of H₂S on the HDO of aliphatic and aromatic oxygenates were attributed to the different reaction mechanisms for oxygen elimination (dehydration, hydrolysis, elimination and direct hydrogenolysis reactions). The different molecular and electronic structures of the aliphatic and aromatic oxygenates are likely the reason for the different reaction mechanisms. Under the identical conditions, phenol was less reactive than aliphatic oxygenates on the sulphided catalysts. In contrast to the situation in the HDO of aliphatic oxygenates, the NiMo catalyst was less active for the HDO of phenol than was the CoMo catalyst.

This work illustrates that the composition of biofuels determines the overall performance of the HDO process and the effect of sulphiding agent on the HDO. The HDO performance may be lower for wood-based biofuels, which contain mainly aromatic oxygenates, than for vegetable oils and animal fats, which contain aliphatic oxygenates. This conclusion further implies that operating conditions in an industrial process need to be more severe for upgrading of wood-based biofuels than upgrading of vegetable oils and animal fats. The addition of a sulphiding agent to the HDO feed will probably affect the total HDO of wood-based biofuels negatively and that of vegetable oils and animal fats positively.

Preface

The experimental work described in this thesis was performed in the Laboratory of Industrial Chemistry at Helsinki University of Technology between August 2001 and March 2006. The financial support provided by Neste Oil Co., Fortum Co. and Helsinki University of Technology are gratefully acknowledged.

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Espoo, May 2007

O. İlke Şenol

List of publications

This thesis is based on the following publications, which are referred to in the text by the corresponding Roman numerals (Paper I-V):

- I. Şenol, O.İ., Viljava, T.-R., Krause, A.O.I., Hydrodeoxygenation of Methyl Esters on Sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ Catalysts, *Catal. Today* **100** (2005) 331-335.
- II. Şenol, O.İ., Viljava, T.-R., Krause, A.O.I., Hydrodeoxygenation of Aliphatic Esters on Sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ Catalyst: The Effect of Water, *Catal. Today* **106** (2005) 186-189.
- III. Şenol, O.İ., Ryymin, E.-M., Viljava, T.-R., Krause, A.O.I., Reactions of Methyl Heptanoate Hydrodeoxygenation on Sulphided Catalysts, *J. Mol. Catal. A: Chem.* **268** (2007) 1-8.
- IV. Şenol, O.İ., Viljava, T.-R., Krause, A.O.I., Effect of Sulphiding Agents on the Hydrodeoxygenation of Aliphatic Esters on Sulphided Catalysts, *Appl. Catal. A: Gen.* **326** (2007) 236-244.
- V. Şenol, O.İ., Ryymin, E.-M., Viljava, T.-R., Krause, A.O.I., Effect of Hydrogen Sulphide on the Hydrodeoxygenation of Aromatic and Aliphatic Oxygenates on Sulphided Catalysts, *J. Mol. Catal. A: Chem.* **277** (2007) 107-112.

Author's contribution

İlke Şenol's contribution to the appended publications:

- I. He planned and carried out the major part of the experiments. He interpreted the results and wrote the manuscript together with the co-authors.
- II. He planned and carried out the major part of the experiments. He interpreted the results and wrote the manuscript together with the co-authors.
- III. He planned and carried out the flow reactor experiments. He was the major contributor in the interpretation of the results and in writing of the manuscript.
- IV. He planned and carried out the experiments. He was the major contributor in the interpretation of the results and in writing of the manuscript.
- V. He defined the research plan and carried out the flow reactor experiments. He was the main contributor in the interpretation of the results and in writing of the manuscript.

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Abbreviations and Symbols

CUS	Coordinatively Unsaturated Sites
DFT	Density Functional Theory
$F_{A,in}$	Inlet molar flow of reactant, mol/h
$F_{A,out}$	Outlet molar flow of reactant, mol/h
F_i	Molar flow of product i , mol/h
FAME	Fatty Acid Methyl Ester
HDM	Hydrodemetallation
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulphurisation
NMR	Nuclear Magnetic Resonance
NTP	Normal Temperature and Pressure (20 °C and 0.101325 MPa)
S_i	Selectivity to product i , %
STM	Scanning Tunnelling Microscopy
X_A	Total conversion of reactant, %

Chapter 1

Introduction

Biomass is an alternative renewable source for the production of traffic fuels. Interest in biomass started with concerns for potential the shortage of crude oil. However, utilisation of biomass has also recently received more attention because of its ecological advantages. Biomass is considered carbon dioxide neutral since using biomass would mean recycling mobile carbon, in contrast to the liberation of fixed carbon resulting from the combustion of fossil fuels [1,2]. In addition, compared to fossil fuels, the sulphur, nitrogen and metal contents of biomass are negligible [2]. Therefore, most countries have introduced dedicated policies for utilisation of biomass. For example, the European Union set as an objective the substitution of biomass-derived fuels (biofuels) for conventional fuels in transport sector with a market share of 5.75% by the end of 2010 [3]. The target for 2005 was a 2% share, and it was not achieved. First generation biofuels, i.e. bioethanol and biodiesel, do not yet replace fossil fuels in sufficiently large amounts. Second generation biofuels has, however, been identified as being particularly promising, but their production technologies need further research and development. Therefore, in order to make the new technologies successful, research and development efforts for preparation of large-scale and cost-competitive biofuels should be given substantial support [4]. Hydrodeoxygenation (HDO) – a process similar to hydrodesulphurisation in oil refining – could provide a possibility for the production of second generation biofuels. A number of processes for the production of second generation biofuels using HDO have already been developed and patented [5-8]. These processes were designed to produce hydrocarbon fractions as

biofuels from vegetable oils, animal fats [5,6,8] and lignin [7]. Feedstocks are processed in several steps including pretreatment for removal of contaminants, depolymerisation in the case of lignin, HDO and isomerisation. Sulphided hydrotreating catalysts such as NiMo/Al₂O₃ and CoMo/Al₂O₃ are utilised in the HDO step.

1.1 Resources of Biomass

There is a wide range of biomass that can be utilised in production of biofuels, such as forestry and agricultural products, including vegetable oils and animal fats, residues and wastes [3,9-11]. The variety and quality of biomass requires its conversion to useful forms prior to utilisation in the transport sector. A number of technologies can be used for the conversion.

Animal fats, vegetable oils (rapeseed, sunflower, palm, soybean, coconut etc.), and sugar and starch crops are used for the production of first generation biofuels. Fats and oils can be converted to biofuels by transesterification, which involves the conversion of triglycerides, which are the main components of fats and oils, with an alcohol to ester and glycerol in the presence of a catalyst [12-14]. The use of methanol in transesterification produces fatty acid methyl esters (FAME). Also known as biodiesel, FAME possesses fuel properties comparable to diesel fuel, and therefore it can be used in diesel engines. When sugar and starch crops are used, the conversion of the raw material, for example by fermentation, produces bioethanol, which can be utilised as a gasoline component [9,11]. Biodiesel and bioethanol are used as blends with conventional fuels at certain fractions.

Wood and triglycerides are the major raw materials for the production of second generation biofuels. Pyrolysis and liquefaction are common thermo-chemical methods for conversion of wood-based biomass to liquid biofuels [1,9,10,15]. These liquids, known as bio-oils, approximate biomass in elemental composition and differ from fossil fuels (Table 1.1) [1,15,16]. Bio-oils are composed of a complex mixture of oxygen-containing compounds [1,9-11,17]. These compounds contribute to the oxygen content of the oil in the form of hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and esters, and aliphatic and aromatic alcohols [1,2,16,18]. In addition, water originating both as moisture in the feedstock and as a product of dehydration reactions in pyrolysis and liquefaction

processes adds to the oxygen content [1,10]. As a result, the total oxygen content of bio-oils can increase up to 50 wt%, depending on the origin of the biomass and the process conditions of pyrolysis and liquefaction, e.g. temperature, residence time and heating rate [16,17]. The oxygen content of bio-oils is a limitation for utilisation as transport fuel since the high oxygen content of bio-oils causes high viscosity, poor thermal and chemical stability, corrosivity and immiscibility with hydrocarbon fuels [1,10,19]. Therefore, bio-oils must be upgraded meaning total or partial reduction of oxygen content [17,20]. When vegetable oils and animal fats are used, the oxygen content can increase up to 10 wt%, and it induces a slightly lower volumetric heating value than conventional diesel fuel [12]. Similarly, upgrading of vegetable oils and animal fats to hydrocarbon components can be considered in the production of second generation biofuels.

Table 1.1. Elemental composition of bio-oil from wood and of heavy fuel oil.

Composition (wt%)	Bio-oil		Heavy Fuel Oil
	Liquefied	Pyrolysed	
Carbon	74.8	45.3	85.0
Hydrogen	8.0	7.5	11.0
Oxygen	16.6	46.9	1.0
Nitrogen	<0.1	<0.1	0.3
Sulphur	<0.1	<0.1	0.5-3.0

1.2 Upgrading Methods and Hydrodeoxygenation

Technologies for upgrading of bio-oils for fuel applications includes physical and chemical/catalytic methods [2,21]. Techniques such as emulsification and solvent addition are physical methods in which biofuels are mixed with diesel oil and solvents, respectively [21]. However, catalytic treatment of biofuels is needed for the total or partial removal of oxygen. Various catalytic upgrading technologies, such as hydrotreating, vapour cracking and steam reforming, have recently been considered in the production of second generation

biofuels [1,2,9,10,17]. Hydrotreating and vapour cracking can be used for production of hydrocarbon components and steam reforming for production of hydrogen.

Hydrotreatment is a well-established refinery practice in which sulphided catalysts are commonly utilised in the presence of hydrogen to remove heteroatoms, such as sulphur, nitrogen, oxygen and metals, from crude oil [21,22]. Thus, hydrodesulphurisation (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetallation (HDM) as well as hydrogenation reactions take place simultaneously during hydrotreating of crude oil [16,22]. Since the oxygen content of crude oil is low, HDO reactions are minor in hydrotreating of different petroleum streams. However, HDO is of utmost importance in hydrotreating of biofuels due to their high oxygen content. Process conditions for HDO of biofuels are similar to those used in refining of crude oil, but the feed is pretreated at low temperature (250 °C) to avoid polymerisation of the oil at the higher temperature of the second stage (400 °C). While the hydrotreating process can provide full deoxygenation of biofuel, partial upgrading is also possible with a mild hydrotreating process with low hydrogen pressure [17,21].

Although sulphided catalysts are traditionally used in hydrotreatment, as mentioned above, application of other types of catalysts, such as solid acid, solid base and metal catalysts, to HDO of biofuels may also be considered. Several studies have been reported regarding the elimination of oxygen from model compounds on catalysts different from conventional sulphided catalysts [23-27]. Recently, the use of such catalysts, in addition to sulphided catalysts, in upgrading of biofuels has been reviewed by Elliott [28]. Utilisation of catalysts other than sulphided catalysts in upgrading process of biofuels is, however, relatively expensive. Extensive application of sulphided catalysts in refinery and well-developed technology therefore make the sulphided catalysts favourable for upgrading of biofuels.

1.3 Sulphided Catalysts

Typical hydrotreating catalysts are composed of molybdenum or tungsten as the active metal, nickel or cobalt as the promoter and the support material such as alumina, silica-alumina, silica or zeolites [16,22,29,30]. The concentration of the metals on the support

usually varies from 8 to 25 wt% for the active metal and from 1 to 4 wt% for the promoter. The choice of catalyst type is important for particular feed and product specifications. The NiMo catalyst is more active for HDN and hydrogenation of aromatic compounds whereas the CoMo catalyst is more active for HDS. As a result, the former catalyst gives relatively high hydrogen consumption, and it is generally preferred for treating unsaturated feeds.

The catalysts are more active in the sulphided form than in the non-sulphided form. Therefore, they are either presulphided with a sulphiding agent or sulphided on stream by adding a sulphiding agent to the feed. The sulphiding agent can be H₂S or a carbon-containing sulphur compound, which can easily decompose under the conditions of hydrotreatment. The sulphidation changes the surface structure of the catalyst, and creates active sites with various configurational and energetic properties. It is generally accepted that coordinatively unsaturated sites (CUS), i.e. sulphur anion vacancies, located at the edge of MoS₂ nanoclusters are the catalytic sites formed in the presence of a sulphiding agent and hydrogen [16,22,29,31]. These sites show Lewis acid character, and they can adsorb atoms with unpaired electrons. Thus, the sulphur anion vacancies can play a role in the rupture of carbon-heteroatom bond. The coordination number of the vacancy sites, however, changes depending on the process conditions. Vacancy sites that are less electrophilic than those for rupture of the carbon-heteroatom bond have been suggested to be active in the hydrogenation reactions [32-35]. Calculations based on density functional theory (DFT) [36,37] have shown that the creation of multiple vacancy sites on sulphided catalysts is energetically unfavourable, however, and therefore reactions that require multiple vacancy sites, such as π -adsorption of aromatic compounds, seem unlikely. Scanning tunnelling microscopy (STM) investigations and DFT calculations have indicated that metallic-like fully saturated molybdenum sites, so-called brim sites, can adsorb molecules, and thus participate in hydrogenation reactions [31,38]. Due to the saturation, the brim sites have been characterised as not interacting strongly with H₂S. The promoter atom (Ni, Co etc.) occupies the edges of MoS₂ phases forming a Ni-Mo-S (Co-Mo-S) structure. Sulphur anion vacancies associated with the promoter atom have been discovered to be more active than those associated with the Mo atom. The role of Ni-Mo-S (Co-Mo-S) structure and the effect of promoter atom have been explained with the significant decrease in the sulphur binding energy [36,39]. In addition, the surface of the

sulphided catalyst bears groups such as S^{2-} , H^+ and SH . The latter two groups show Brønsted acid character, and they provide hydrogen for hydroprocessing reactions.

Oxygen-containing organic compounds and water, present in bio-oils and formed in the HDO process, can modify the sulphide structure of the catalyst. Therefore, activity, stability and selectivity of the catalyst may be negatively affected. The low sulphur content of bio-oils may not be sufficient to maintain the sulphided state of the catalysts, and continuous addition of a sulphiding agent to the reactor may be a reasonable way of maintaining the sulphided state of the catalyst [16,29]. In literature, the addition of a sulphiding agent to the feed has, however, been reported to affect the HDO process differently depending on the feed composition and the process conditions. For instance, the sulphiding agent added to the HDO feed has generally been found to inhibit the HDO of phenolic and furanic compounds on sulphided catalysts [32,33,40-43]. Yet, few studies regarding the HDO of aliphatic oxygenates have showed a promoting effect of the sulphiding agent on HDO [44,45].

1.4 Scope of the Work

The high oxygen content and the variable compositions of bio-oils from different sources cause differences in HDO reactivity of bio-oils. Further, a sulphiding agent added to the HDO feed can affect performance of the catalyst. Therefore, a careful study is required with different catalysts and bio-oil feeds in order to optimise the process parameters for a particular feed and a specified product. For this purpose, understanding the behaviour of different bio-oil components under HDO conditions is of great important.

So far, HDO studies have focused mostly on phenolic and furanic compounds because of their low reactivity and abundance in bio-oils. A few studies regarding the HDO of aliphatic oxygenates on sulphided catalysts have been reported [44-49]. Yet, results from different studies are not mutually consistent due to different experimental conditions. Therefore, investigation of the HDO of different oxygenates under the same conditions seems to be desirable.

The objective of this work was to investigate the HDO of oxygenates having different molecular and electronic structures and to determine the influence of compounds that are

either formed in the HDO process or added to the HDO process feed, such as water and the catalyst sulphiding agents, H₂S and CS₂. Experiments were conducted with commercial NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ hydrotreating catalysts in the gas and liquid phase. Special attention was paid to the HDO of aliphatic oxygenates such as esters, alcohols and carboxylic acids. The HDO of phenol as model aromatic compound was studied in the absence and presence of H₂S under the same conditions of the HDO of aliphatic oxygenates to allow for direct comparison.

Materials and methods used in the experimental work are described in chapter 2. The reactions of aliphatic oxygenates and the effect of additives on these reactions are discussed in chapter 3. The HDO of the aromatic model compound is described in chapter 4, and the results are compared with those of the HDO of aliphatic model compounds in chapter 5. Finally, chapter 6 summarises the conclusions and provides an outlook for future studies.

Chapter 2

Materials and Methods

HDO experiments were carried out in the gas and liquid phase using a tubular flow and a batch reactor, respectively. This chapter presents the details of the materials and procedures applied in the experimental work.

2.1 Catalysts and Chemicals

Table 2.1 lists the gases and chemicals used in the experiments. All the gases and chemicals were used as received. The esters, heptanol and heptanoic acid were confirmed to be water-free by NMR analysis.

The catalysts were commercial NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ hydrotreating catalysts containing 12-16 wt% molybdenum and 3-5 wt% nickel or cobalt on γ -alumina. After the catalyst samples were crushed and sieved to a particle size of 0.59-0.75 mm, they were used in either non-sulphided or sulphided form. In addition, experiments with a pure γ -alumina support (Akzo, γ -Al₂O₃ 001/1.5 E) were performed for investigation of the reactions of aliphatic esters on the support, and the results were reported in Paper I. The alumina support was crushed and sieved to a particle size of 0.42-0.59 mm.

Table 2.1. Gases and Chemicals used in the hydrodeoxygenation experiments.

	Supplier	Purity	Paper
<i>Gases</i>			
Hydrogen	Aga	99.999%	I-V
Nitrogen	Aga	99.999%	I-V
0.25 and 5 vol% H ₂ S/H ₂	Aga	99.999%	I-V
<i>Chemicals</i>			
Methyl hexanoate (reactant) ^a	Fluka	>99%	I
Methyl heptanoate (reactant)	Fluka and Merck	>99% and >98%	I-IV
Ethyl heptanoate (reactant) ^a	Aldrich	99%	II,IV
1-Heptanol (reactant)	Aldrich	98%	III,IV
<i>n</i> -Heptanoic acid (reactant)	Aldrich	99%	I,III,IV
Phenol (reactant)	J.T. Baker	Lab. grade	V
Cyclohexanone (reactant) ^a	Fluka	>99%	V
Cyclohexanol (reactant)	Aldrich	99%	V
Benzene (reactant) ^b	Fluka	>99%	V
CS ₂ (additive)	Merck	>99%	IV
<i>m</i> -Xylene (solvent)	Fluka and Merck	>99% and >98%	I-V
<i>n</i> -Decane (standard) ^b	Sigma	>99%	III,V
Cumene (GC standard) ^a	Fluka	>98%	I-V
<i>n</i> -Dodecane (GC standard) ^b	Merck	>99%	III,V

^a Used only in the flow reactor experiments.

^b Used only in the batch reactor experiments.

2.2 Hydrodeoxygenation Experiments in Gas Phase

Gas phase experiments were carried out with a tubular flow reactor system (Figure 2.1). The liquid and gas feeds were regulated with mass flow controllers. Both feed lines were heated to 190 °C and merged upstream of the reactor. The reactor was made of stainless steel with dimensions of 10 mm inside diameter and 380 mm length. An electrical furnace heated the reactor. The catalyst was packed between two layers of silicon carbide (1-3

mm), and the catalyst bed was located in the middle of the reactor. The temperature of the catalyst bed was measured with a thermocouple in the reactor. The outlet stream of the reactor was cooled in an ice bath. The liquid phase was withdrawn for offline analysis, while the gas outlet stream was analysed online with a gas chromatograph.

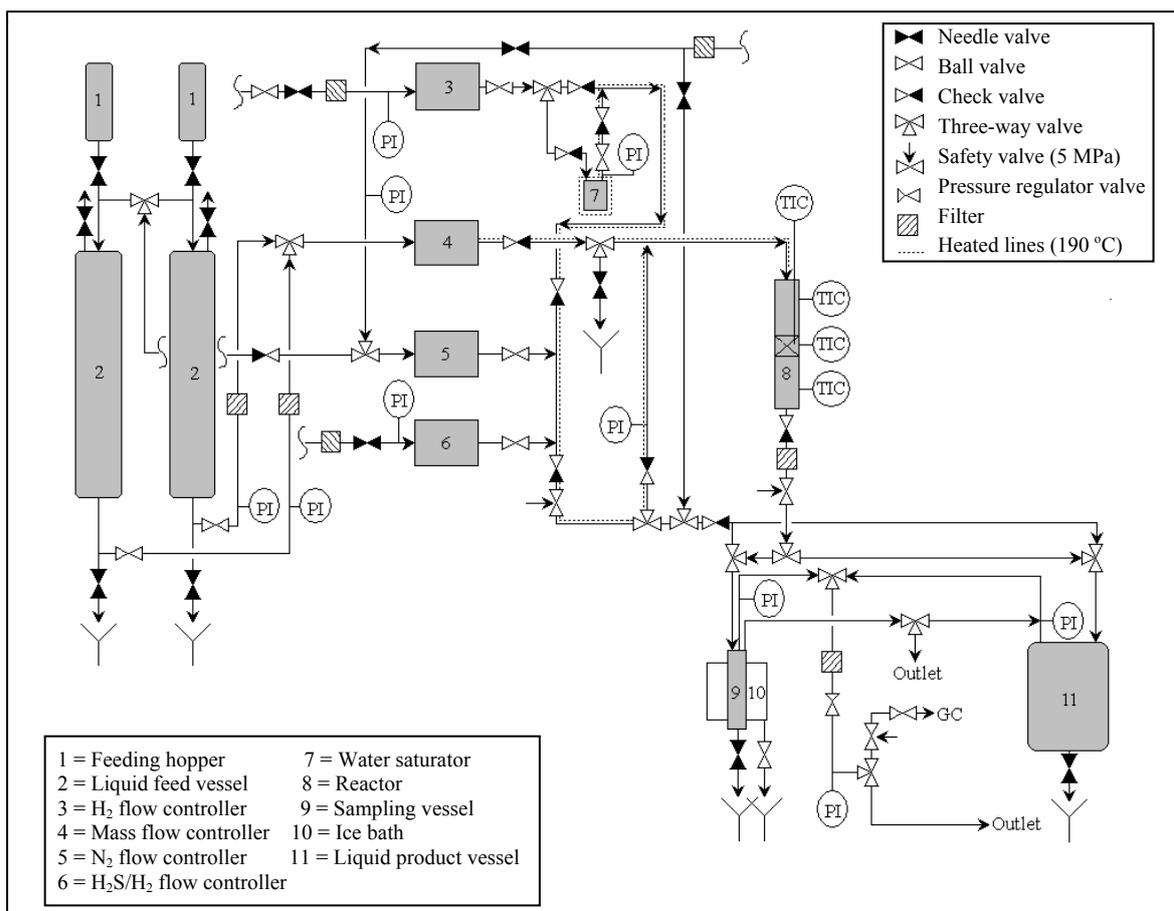


Figure 2.1. Flow reactor system used for the gas phase hydrodeoxygenation experiments.

2.2.1 Catalyst pretreatment

The catalyst loading in the reactor was 0.5 g. Additional experiments with heptanol as the model reactant were performed with different catalyst loadings (0.2-0.5 g), as shown in Table 1 in Paper III. A batch of the catalyst was activated at 400 °C under atmospheric pressure. After a 2 h calcination period under nitrogen flow, the catalyst sample was

presulphided under 5 vol% H₂S/H₂ mixture flow for 4 h. The flow rate of nitrogen and the H₂S/H₂ mixture during the activation period was 2.5 l/h (NTP). Following the presulphidation period, reactor pressure was increased to about 0.5 MPa with 5 vol% H₂S/H₂ mixture, and the temperature was reduced to the reaction temperature (250, 275 or 300 °C). The system was left overnight under these conditions. Experiments with the alumina support and the non-sulphided catalysts were performed at 300 °C after the calcination step.

2.2.2 Catalytic experiments

Experiments were performed under 1.5 MPa total pressure and initiated after the reactor was flushed shortly with hydrogen to remove H₂S. Total flow rate of the gas feed in the experiments was 2 l/h (NTP). The liquid feed containing 3 wt% reactant in *m*-xylene was fed at a rate of 10 g/h (NTP). In the experiments with heptanol as the model compound, alcohol composition of the liquid feed was varied between 3 and 15 wt% (Paper III, Table 1). The first liquid sample was withdrawn from the sampling vessel after a 2 h stabilisation period. A standard run lasted 6.5 h, and sampling was repeated every 30 min. The reactor was cooled under nitrogen flow after each run, and the catalyst was separated for analysis of the sulphur and carbon contents.

The calculated concentrations (mol-ppm) of added water, H₂S and CS₂ in the reactor are presented in Table 2.2. In the study of the effect of water on the reactions of the aliphatic esters, water could not be added to the liquid feed due to its low solubility in *m*-xylene. Instead, it was added to the gas feed by passing the hydrogen stream through a water saturator filled with distilled water and located upstream of the reactor (Figure 2.1). The temperature of the saturator was controlled with a heater, and the amount of water in the feed was estimated from the saturated vapour pressure of water at the corresponding temperature.

Catalyst deactivation was studied separately with methyl heptanoate by conducting experiments for 15 h. Reactions of the esters in the absence of a catalyst were examined at 250 and 300 °C with methyl hexanoate and methyl heptanoate as the model compounds.

Table 2.2. Concentrations (mol-ppm) of water, H₂S and CS₂ added to the reactor.

Paper	II	IV		V
Additive	Water:H ₂ S	H ₂ S	CS ₂	H ₂ S
Reactant	(mol-ppm:mol-ppm)	(mol-ppm)	(mol-ppm)	(mol-ppm)
Methyl heptanoate	750:0, 1800:0, 5000:0, 18,600:0, 18,600:830, 0:1000	140, 500, 1000, 24,000 ^a	740, 2200, 3700	-
Ethyl heptanoate	5000:0, 18,600:0, 18,600:830	140, 1000	-	-
1-Heptanol	-	4500, 7000	-	-
<i>n</i> -Heptanoic acid	-	250, 1675	-	-
Phenol	-	-	-	60, 1200, 2600, 12,000, 24,000 ^b
Cyclohexanol	-	-	-	3800 ^b

^a Experiments were carried out with the NiMo/ γ -Al₂O₃ catalyst.

^b Experiments were carried out with the CoMo/ γ -Al₂O₃ catalyst.

2.3 Hydrodeoxygenation Experiments in Liquid Phase

Liquid phase experiments were performed in a 50-ml batch reactor equipped with a fixed-catalyst basket and a magnetic stirrer. The HDO of the aliphatic oxygenates were studied on the NiMo catalyst and the HDO of the aromatic and cyclic compounds on both NiMo and CoMo catalysts. Preliminary experiments in the batch reactor showed that a catalytic regime was obtained at a stirring speed of 1000 rpm, and hence the mixing speed was kept constant at 1000 rpm during the catalyst pretreatment and reactions.

2.3.1 Catalyst pretreatment

After a batch of catalyst (0.5 g) was packed into the catalyst basket, the catalyst was activated at 350 °C under atmospheric pressure. The catalyst was first calcined for 2 h

under 6 l/h (NTP) nitrogen flow. It was then presulphided for 2 h under 5 vol% H₂S/H₂ mixture flow at a rate of 3 l/h (NTP). Following the presulphidation period, the reactor was cooled under 6 l/h (NTP) nitrogen flow to the reaction temperature (250 °C).

2.3.2 Catalytic experiments

Experiments under 7.5 MPa hydrogen pressure were started by feeding 16 ml reaction mixture, which contained the reactant and *n*-decane as the standard in *m*-xylene. The composition of the reactant in the reaction mixture was 5 wt% for methyl heptanoate, 2 wt% for heptanol, 2 wt% for heptanoic acid, 3 wt% for phenol, 2 wt% for cyclohexanol and 1 wt% for benzene. The reaction time was varied between 5 and 180 min, and the liquid samples (about 100 mg) were withdrawn from the sampling valve located at the bottom of the reactor. The sampling line was purged with about 250 mg reaction mixture before each sample was taken out. Hydrogen was not added to the reactor during the runs. In order to avoid excessive pressure drop in the reactor due to sampling, only five samples were withdrawn in each run. Thus, the vapour-liquid phase equilibrium was assumed to be unaffected by the pressure change in the reactor, and the results were discussed on the basis of the liquid phase compositions. Reactions of methyl heptanoate in the absence of a catalyst were studied separately.

2.4 Analyses

An HP 6890 series Hewlett-Packard gas chromatograph was used to analyse the liquid samples. The chromatograph was equipped with a flame ionisation detector and an HP-1 column of dimensions 60 m x 0.25 mm and 1 µm film thickness. The response factors for the reactants and the products were determined and checked regularly with the calibration solutions of known concentrations. A GC/MS was used to determine the reaction products in trace amounts. The gas outlet stream of the flow reactor was analysed qualitatively with an online Hewlett-Packard gas chromatograph (HP 5890A) equipped with a thermal conductivity detector. The results reported in Paper II were obtained by using a packed column of activated carbon with 2% squalane. In the studies reported in Paper III, IV and V, the column was replaced with an HP-PLOT/U column of dimensions 30 m x 0.32 mm and 10 µm film thickness to improve the analysis method. The gas phase of the batch

reactor was probed for CO₂, CO and H₂S with Dräger tubes at the end of each experiment with aliphatic oxygenates.

The sulphur and carbon contents of the catalysts were analysed with a sulphur-carbon analyser (LECO, SC-444 series). Before the analyses, the catalyst samples were dried overnight in an oven under air at 100 °C.

2.5 Definitions

In the flow reactor experiments, total conversion of a reactant, X_A , and the selectivity to product i , S_i , were calculated with:

$$X_A = \frac{F_{A,in} - F_{A,out}}{F_{A,in}} \times 100\% \quad (1)$$

$$S_i = \frac{F_i}{F_{A,in} - F_{A,out}} \times 100\% \quad (2)$$

The HDO conversion of a reactant was defined by the fraction of reactant converted to hydrocarbons. The reaction yield of each product was equal to the product of the total conversion and the selectivity divided by a hundred. In the batch reactor experiments, total and HDO conversions, selectivities and yields were calculated by using reactant and product molar concentrations.

Chapter 3

Reactions of Aliphatic Oxygenates

A reaction scheme for the HDO of aliphatic esters was proposed in Paper I. However, it became possible to demonstrate the scheme in detail in Paper III after a comprehensive investigation of the reactions with alcohol and carboxylic acid, which were formed as intermediates in the HDO of aliphatic esters. Water is formed in the HDO reactions, and the addition of a sulphiding agent to the HDO feed is typically required to maintain the sulphided state of the catalysts. The degree of effect of water and sulphiding agent may, however, vary depending on factors such as type of catalyst, composition of feed, and amounts of water and sulphiding agent. Based on results obtained from the model aliphatic oxygenates, this chapter explains the reactions in the proposed scheme and the effect of water and H₂S on them.

3.1 Reaction Products

Reactions of the aliphatic oxygenates on the sulphided catalysts produced hydrocarbons, and oxygen- and sulphur-containing compounds. Table 3.1 shows the products detected in liquid samples obtained after reactions of the aliphatic oxygenates on both catalysts. It is worth noting that the sulphur-containing compounds in Table 3.1 were also formed in the absence of sulphiding agents in the feed. Formation of carbon oxides, CO₂ and CO, in the reactions of the model esters and carboxylic acid was detected in the analysis of the gas outlet stream, revealing the removal of oxygen as carbon oxides in addition to water in the HDO of aliphatic oxygenates. Methane and ethane depending on the alkyl part of the esters

and, in the batch reactor studies, H₂S were detected in the gas outlet stream. No gaseous products were detected in the reactions of heptanol.

Reactions of methyl esters on the non-sulphided catalysts produced hydrocarbons and oxygen-containing compounds. Hydrocarbons were the same with those formed on the sulphided catalysts, and oxygen-containing compounds were only alcohols and carboxylic acid, as seen in Table 3.1. All the products were formed in trace amounts, however.

Table 3.1. Reaction products of aliphatic oxygenates detected in the liquid samples.

Reactant	Products		
	Hydrocarbons	Oxygen-containing compounds	Sulphur-containing compounds
Methyl hexanoate	C ₅ ^a , C ₆ ^b	methanol, 1-hexanol, hexanoic acid	- ^c
Methyl heptanoate	C ₆ ^b , C ₇ ^d	methanol, 1-heptanol, <i>n</i> -heptanoic acid, heptyl heptanoate, heptanal, dimethyl and diheptyl ether	1-methanethiol, 1-hexanethiol, 1-heptanethiol, dimethyl and diheptyl sulphide, H ₂ S
Ethyl heptanoate	C ₆ ^b , C ₇ ^d	ethanol, 1-heptanol, diethyl ether, heptanal, <i>n</i> -heptanoic acid, heptyl heptanoate	1-hexanethiol, 1-heptanethiol, diethyl and diheptyl sulphide, H ₂ S
1-Heptanol	C ₇ ^d	diheptyl ether	1-heptanethiol, diheptyl sulphide ^e
<i>n</i> -Heptanoic acid	C ₆ ^b , C ₇ ^d	1-heptanol, heptyl heptanoate, heptanal, diheptyl ether	1-hexanethiol ^e , 1-heptanethiol

^a *n*-pentane, 1-pentene and *cis/trans*-2-pentene.

^b *n*-hexane, 1-hexene, *cis/trans*-2-hexene and *cis/trans*-3-hexene.

^c Not analysed.

^d *n*-heptane, 1-heptene, *cis/trans*-2-heptene and *cis/trans*-3-heptene.

^e Not detected in the batch reactor studies.

Experiments reported in Paper I showed no reactions of methyl esters at 300 °C in the absence of a catalyst. With the improvement of the analysis method, however, a slight conversion of methyl heptanoate (<5%) at 250 °C was revealed (Paper III). The reaction products were methanol, heptanol and heptanoic acid. The carboxylic acid was detected only in the batch reactor studies.

When the activity of the alumina support was examined in the flow reactor at 300 °C, total conversion of the methyl esters was about 13%, and the reaction products were the alcohols and carboxylic acid, as seen in Table 3.1. The activity of the support was attributed to its acidity [50-52].

3.2 Reactions of Aliphatic Esters

A significant part of the products in the liquid samples included hydrocarbons and some of the oxygen-containing compounds. Concentrations of these major products formed in the reactions of methyl heptanoate changed as a function of time in the batch reactor, as seen in Figure 3.1. Total conversion of the ester after 60 min was 93%. Clearly, heptanoic acid was formed as a primary product in the reactions of the ester. In the experiments with heptanoic acid, the concentrations of hydrocarbons, heptanol and heptyl heptanoate changed as a function of time in the same way as they did in the experiments with methyl heptanoate (Paper III, Fig. 6). Accordingly, it was concluded that heptane and hexane were the end products, while heptenes, hexenes, heptanol and heptyl heptanoate were the intermediates in the reactions of the ester and carboxylic acid compounds.

When the reactions of heptanol were studied in the flow reactor using the same amount of catalyst and reactant as in the experiments with the esters, complete conversion of heptanol was observed. Hence, in order to detect reaction intermediates, reactions of heptanol were studied by varying the amount of catalyst and reactant to obtain incomplete conversion (Paper III, Table 1). Thus, product distributions were obtained at various space times, which were defined by the ratio of the amount of catalyst to the molar flow of heptanol. Product distribution as a function of space time (Paper III, Fig. 4) revealed that heptenes and diheptyl ether were formed as intermediates and heptane as the end product in the reactions of heptanol on the sulphided catalysts.

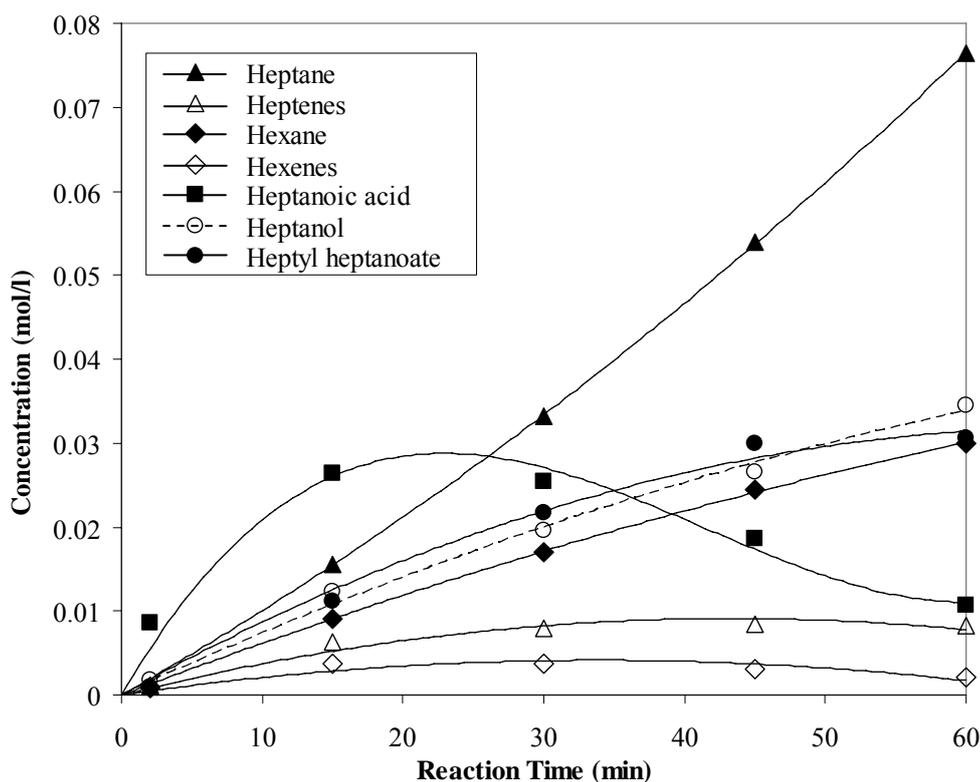


Figure 3.1. Concentration profiles of the major products formed in the reactions of methyl heptanoate on sulphided NiMo/ γ -Al₂O₃ catalyst at 250 °C under 7.5 MPa pressure in the batch reactor (Paper III).

Figure 3.2 depicts the proposed scheme for the HDO of methyl heptanoate and ethyl heptanoate on the basis of the detected products and their concentration profiles. The scheme for the reactions of methyl hexanoate is identical except that heptanol and heptanoic acid in Figure 3.2 should be replaced with hexanol and hexanoic acid, respectively, and similarly C₇ and C₆ hydrocarbons with C₆ and C₅ hydrocarbons.

Heptanol and heptanoic acid appear as the primary products of the esters in Figure 3.2. In particular, the concentration profile of the acid in Figure 3.1 suggested a fast formation rate for the acid. Reactions of the methyl esters on the alumina support and in the absence of a catalyst clearly indicated formation of the acid, as mentioned above, but the formation of acid in a trace amount could not sufficiently explain the fast formation rate of the acid. It is known that acid-catalysed reactions can take place on sulphided catalysts [22], and acid-

catalysed hydrolysis reactions of esters yields carboxylic acids [53]. Thus, it was suggested that the carboxylic acid could be formed by the hydrolysis of the esters on the sulphided catalysts. It is worth noting that water is needed for the hydrolysis reaction. Since the catalyst pretreatment presumably removed water from the catalyst pores, the hydrolysis reaction supposedly became significant after formation of water by, for example, the reactions of carboxylic acid (Figure 3.2) that could be formed due to the activity of alumina support.

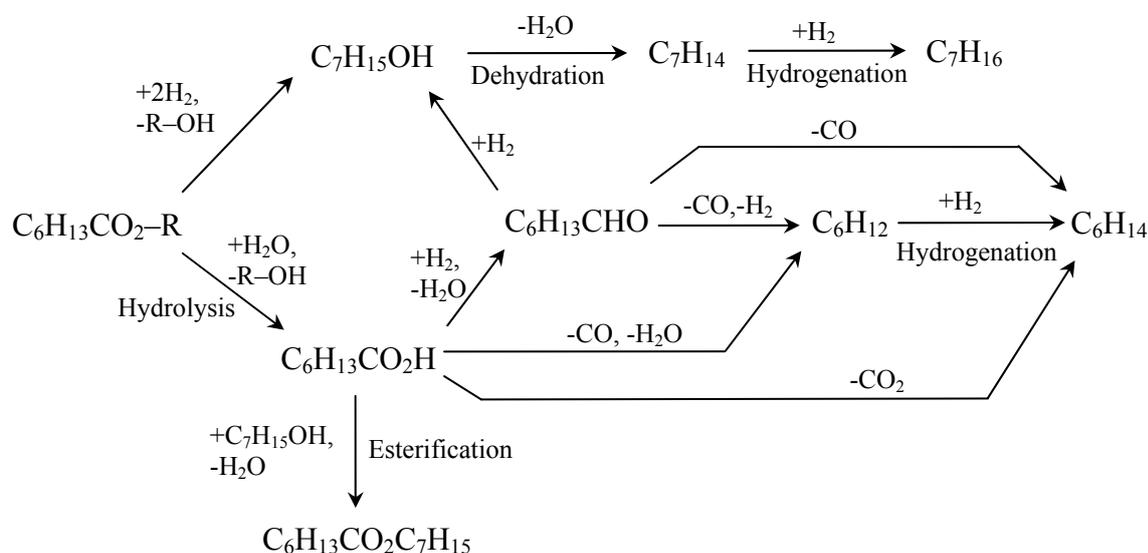


Figure 3.2. Reactions of methyl heptanoate (R = CH₃) and ethyl heptanoate (R = C₂H₅) on sulphided catalysts (Paper IV).

The proposed reactions for the intermediate carboxylic acid lead to formation of aldehyde, ester and C₆ hydrocarbons. Aldehyde was not detected in the study reported in Paper I, and formation of an intermediate aldehyde was confirmed after improvement of the analysis method (Paper III). Formation of the heptyl ester was explained in terms of reverse of the hydrolysis reaction, i.e. esterification reaction, of heptanol and heptanoic acid. In the study of deoxygenation of stearic acid on various supported metal catalysts [24], Snåre et al. found that the acid was converted to saturated and unsaturated hydrocarbons by decarboxylation and decarbonylation reactions in which carbon oxides (CO₂ and CO) were formed as side products. Similarly, formation of carbon oxides detected in the reactions of

the esters and the acid in this work were explained by the conversion of the acid to C₆ hydrocarbons. The removal of CO and water from the heptanoic acid molecule yielded hexenes, and the elimination of CO₂ from the acid produced hexane (Figure 3.2). An abstraction of CO from the aldehyde molecule could also yield C₆ hydrocarbons. Thermodynamic calculations using HSC Chemistry[®] software [54] revealed that the formation reactions of carbon oxides and hydrocarbons from the acid and the aldehyde are not equilibrium-limited under the conditions studied (Paper III, Table 3).

Formation of heptenes was explained by the dehydration reaction, which principally occurs by the acid-catalysed E₁ and E₂ mechanisms [55,56]. Nevertheless, since E₁ mechanism leads to formation of an energetically unstable primary carbenium ion, as shown in Figure 3.3a, and the acidity of sulphided catalysts is not high enough to produce a primary carbenium ion [57], E₁ mechanism is unlikely. Formation of 1-heptene was, therefore, explained by the E₂ elimination mechanism (Figure 3.3a), and the formation of *cis/trans*-2-heptene and *cis/trans*-3-heptene by the acid-catalysed isomerisation reactions of 1-heptene to form more stable internal heptenes [53]. The formation of heptane may be explained by the hydrogenation of heptenes and/or the direct hydrogenolysis of heptanol, which means cleavage of the C-O bond and simultaneous hydrogenation. The NiMo catalyst, in accordance with the high hydrogenation capacity [22,30], was selective to saturated hydrocarbons and the CoMo catalyst to unsaturated hydrocarbons as further discussed in section 3.3.1. Therefore, it was concluded that hydrogenation of heptenes was the main route for the formation of heptane. The catalytic sites for the formation of C₇ hydrocarbons were proposed to be the sulphur anion vacancies (CUS) as they show Lewis acid character [16,22,29].

Formation of ethers and sulphur-containing compounds in the absence of a sulphiding agent in the feed indicated a possible role of nucleophilic substitution reactions, which, in principle, occur by S_N1 and S_N2 mechanisms. Since no sulphiding agent was added to the reactor, the presence of reactive (weakly bonded) sulphur species on catalysts were proposed to participate in the formation of sulphur-containing compounds. However, S_N1 mechanism is unlikely since it leads to an energetically unstable primary carbenium ion as E₁ mechanism does (Figure 3.3b). This conclusion was further supported by the fact that S_N1 mechanism would lead to 2-heptanethiol, which was not detected in the analyses

(Figure 3.3b). Sulphur-containing compounds and ethers were detected in trace amounts. It is likely that sulphur-containing compounds were quickly converted to hydrocarbons and H_2S under the studied conditions. Similarly, ethers could form hydrocarbons and water. The formation of sulphur-containing compounds by nucleophilic substitution reactions has been reported in the HDN of aliphatic and cyclic alkylamines on sulphided catalysts [57-61].

In summary, hydrogenation and acid-catalysed reactions (hydrolysis, esterification, dehydration, E_2 elimination, $\text{S}_{\text{N}}2$ nucleophilic substitution) were concluded to play a major role in the HDO of aliphatic oxygenates on the sulphided catalysts.

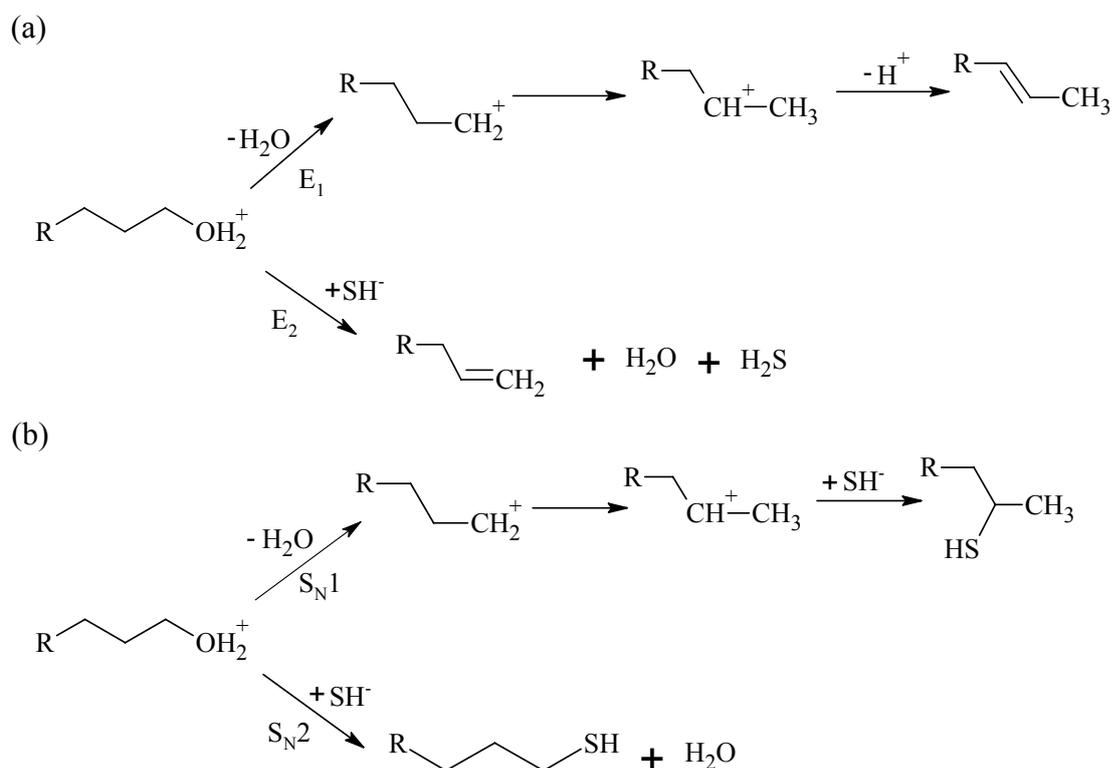


Figure 3.3. Acid-catalysed (a) elimination and (b) nucleophilic substitution mechanisms of 1-heptanol ($\text{R}=\text{C}_4\text{H}_9$, Paper II).

3.3 Effects of additives on catalyst activities and product distributions

3.3.1 Catalyst activity and stability in the absence of additives

When the activity of the catalysts was probed for 15 h in the flow reactor, total conversion of methyl heptanoate on both catalysts reached a pseudo steady-state level after a sharp decrease in the first 4 h (Paper III, Fig. 1). Furthermore, selectivities to hydrocarbons and, as a result, the molar ratios of C₇ to C₆ hydrocarbons changed as a function of time. For example, the molar ratio in the reactions of methyl heptanoate increased in the first 4 h from 1.0 to 1.5 on the NiMo catalyst and from 1.4 to 2.1 on the CoMo catalyst. The molar ratios of saturated to unsaturated hydrocarbons decreased as a function of time on the NiMo catalyst. All these results clearly indicated initial deactivation of the catalysts, which is typically seen in hydroprocessing catalysts during commercial operation [29]. The increasing molar ratio of C₇ to C₆ hydrocarbons further suggested the deactivation of the routes to C₆ hydrocarbons to be faster than the routes to C₇ hydrocarbons. Likewise, the decreasing saturated to unsaturated hydrocarbon ratios on the NiMo catalyst revealed the effect of catalyst deactivation on the hydrogenation reactions. Owing to the deactivation, the results were discussed on the basis of the average conversion, selectivity and yield values calculated after the pseudo steady-state was reached in a standard run (usually between 4 and 6.5 h).

Coke formation and desulphurisation of the sulphided catalysts are known causes of catalyst deactivation in hydroprocessing [16,22,29]. The sulphur content of the catalysts was 7.0±0.3 wt% after presulphidation in the flow reactor and 5.8±0.3 wt% after presulphidation in the batch reactor. In the flow reactor studies with the esters and the carboxylic acid, the carbon-free sulphur content of the catalysts decreased to 5.0-6.0 wt%, clearly indicating desulphurisation of the catalysts. Since no sulphiding agent was added to the feed, catalyst desulphurisation further substantiated the conclusion that reactive sulphur species on the catalyst surface play a role in the formation of sulphur-containing compounds. The carbon-free sulphur content of the catalysts, however, did not change significantly in the batch reactor studies. The carbon content of both catalysts increased in all experiments to 4.5-7.5 wt%. These variations in the sulphur and carbon contents of the catalysts were, at least partially, responsible for the catalyst deactivation.

Table 3.2 shows total and HDO conversions of the esters and the carboxylic acid at pseudo steady-state in the flow reactor. The results for heptanol in the presence of different amounts of catalyst and reactant are presented in Table 1 in Paper III. Under identical conditions, activity of the NiMo catalyst was higher than that of the CoMo catalyst as the total and HDO conversions were higher on the NiMo catalyst than on the CoMo catalyst (Table 3.2). The non-sulphided catalysts were clearly less active than the sulphided catalysts. In the batch reactor studies, total and HDO conversions of methyl heptanoate on the sulphided NiMo catalyst at 250 °C were complete in 2.5 and 3 h, respectively. Similarly, total and HDO conversions of heptanoic acid were complete in 45 min and 1 h.

Table 3.2. Total and HDO conversions of aliphatic oxygenates on NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts at pseudo steady-state in the flow reactor studies.

Catalyst Form		NiMo/ γ -Al ₂ O ₃				CoMo/ γ -Al ₂ O ₃			
		Oxide	Sulphided			Oxide	Sulphided		
Temp. (°C)		300	250	275	300	300	250	275	300
Methyl hexanoate	Total ^a	34	71	~100	~100	15	41	79	~100
	HDO ^b	15	60	90	~100	<2	32	70	~100
Methyl heptanoate	Total ^a	43	78	~100	~100	12	46	81	~100
	HDO ^b	8	67	~100	~100	<2	34	65	~100
Ethyl heptanoate	Total ^a	-	72	-	-	-	49	-	-
	HDO ^b	-	66	-	-	-	37	-	-
<i>n</i> -Heptanoic acid	Total ^a	-	90	-	-	-	47	-	-
	HDO ^b	-	82	-	-	-	34	-	-

^a Total conversion of reactant (%).

^b Fraction of reactant converted to hydrocarbons (HDO conversion, %).

Figure 3.4 depicts the selectivities to the major products formed in the reactions of methyl heptanoate, ethyl heptanoate and heptanoic acid on the sulphided catalysts at 250 °C in the flow reactor studies. The main products were heptane on the NiMo catalyst and heptenes

on the CoMo catalyst. The sulphided NiMo catalyst, in accordance with its high hydrogenation activity [22,30], was selective to the saturated hydrocarbons under all the studied conditions in the absence of a sulphiding agent. The sulphided CoMo catalyst, on the other hand, was selective to saturated hydrocarbons only at complete conversion, which was achieved at 300 °C.

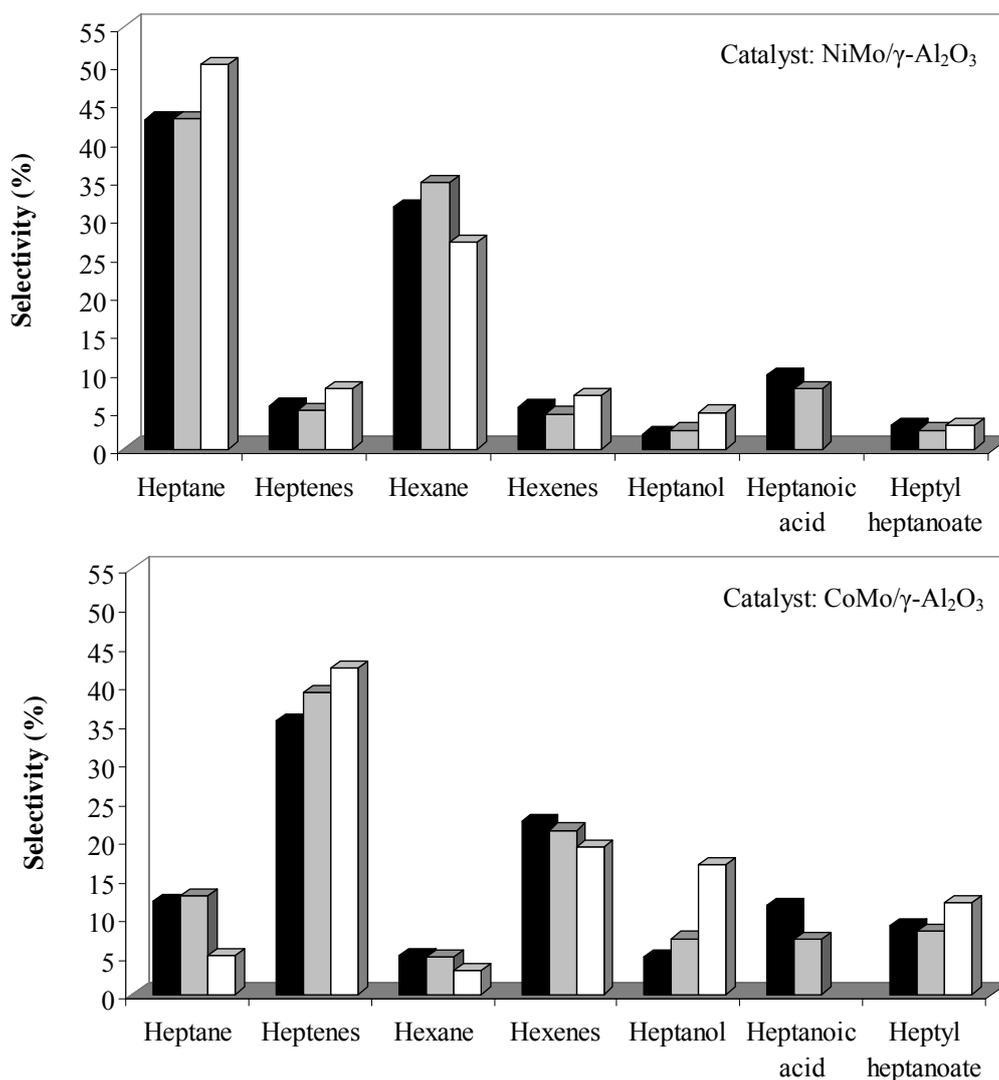


Figure 3.4. Selectivities to the major products formed in the reactions of methyl heptanoate (■), ethyl heptanoate (▣) and heptanoic acid (□) on sulphided catalysts in the gas phase at 250 °C under 1.5 MPa pressure (see Table 3.2 for conversions).

3.3.2 Effect of water

The addition of water in the feed reduced total conversion of methyl heptanoate and ethyl heptanoate on both catalysts, as seen in Figure 3.5. Similarly, HDO conversion of the esters on both catalysts dropped when water was added. For instance, the addition of 18,600 ppm water to the feed reduced the HDO conversion of methyl heptanoate from 67 to 43% on the NiMo catalyst and from 34 to 19% on the CoMo catalyst. Accordingly, it was concluded that water inhibits the HDO of aliphatic esters.

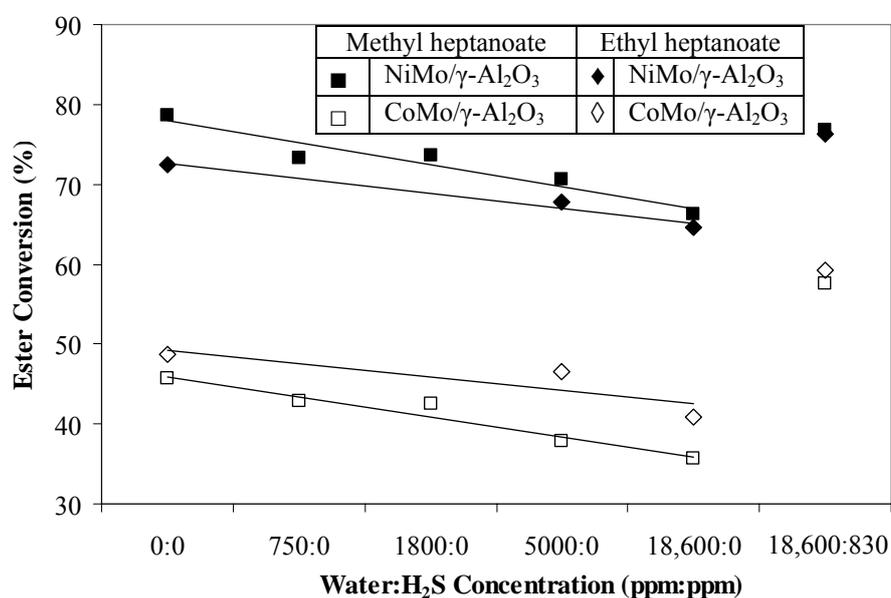


Figure 3.5. Effect of addition of water on total conversion of methyl heptanoate and ethyl heptanoate on sulphided catalysts in the gas phase at 250 °C under 1.5 MPa pressure.

On both catalysts, the addition of water decreased particularly the yield of C₆ hydrocarbons (Paper II, Fig. 1), indicating the inhibition of mainly the routes to C₆ hydrocarbons. In the mean time, the yields of heptanol and heptanoic acid increased. When water was added, the molar ratios of saturated to unsaturated hydrocarbons decreased on the NiMo catalyst, but they were not affected on the CoMo catalyst (Paper II, Table 1). Evidently, the addition of water inhibited the hydrogenation reactions on the NiMo catalyst, but a similar effect was not apparent on the CoMo catalyst.

3.3.3 Effect of sulphiding agents

Total conversion of the esters and the carboxylic acid showed a similar trend as a function of time with the addition of H₂S and CS₂ as was seen in their absence. Evidently, the addition of a sulphiding agent did not prevent the catalyst deactivation. The carbon content of the catalysts increased in the presence of the sulphiding agents up to 7.0 wt% (Paper IV, Table 1). No correlation was found between the increases and the concentration of sulphiding agent in the feed, but the carbon content of the catalysts were higher with the addition of CS₂ than with the addition of H₂S. The sulphur content of the NiMo catalyst was nearly maintained at its original level in the presence of a sulphiding agent, but that of the CoMo catalyst decreased regardless of the concentration of sulphiding agent in the feed (Paper IV, Table 1). Accordingly, the catalyst deactivation in the presence of a sulphiding agent was attributed to the increase in the carbon content of the catalysts and to the decrease in the sulphur content of the CoMo catalyst.

On both catalysts, the addition of H₂S enhanced total and HDO conversions of the aliphatic esters (Figure 3.6a). Similar results were obtained in the reactions of heptanol and heptanoic acid (Paper IV, Table 2). Although a high concentration of water (18,600 ppm) was added simultaneously, the addition of 830 ppm H₂S maintained the conversions of the esters on the NiMo catalyst, and it even enhanced them on the CoMo catalyst, as shown in Figure 3.5. Thus, H₂S effectively compensated the inhibition by water. All these results clearly indicated that H₂S had a promoting effect on the HDO of the aliphatic oxygenates. The presence of a sulphiding agent has been reported to increase especially the Brønsted acidity of sulphided catalysts [62-64]. Accordingly, the promoting effect of H₂S was attributed to enhancement of the acid-catalysed reaction due to the increased catalyst acidity. Several studies on the HDN of nitrogen-containing compounds, such as aliphatic and cyclic alkylamines and indole, have demonstrated that the addition of a sulphiding agent enhanced the HDN of nitrogen-containing compounds on sulphided NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts as a result of the increased Brønsted acidity [35,57,60,61]. In this respect, the promotion of the HDO of aliphatic oxygenates by H₂S may be compared with the promotion of the HDN of nitrogen-containing compounds.

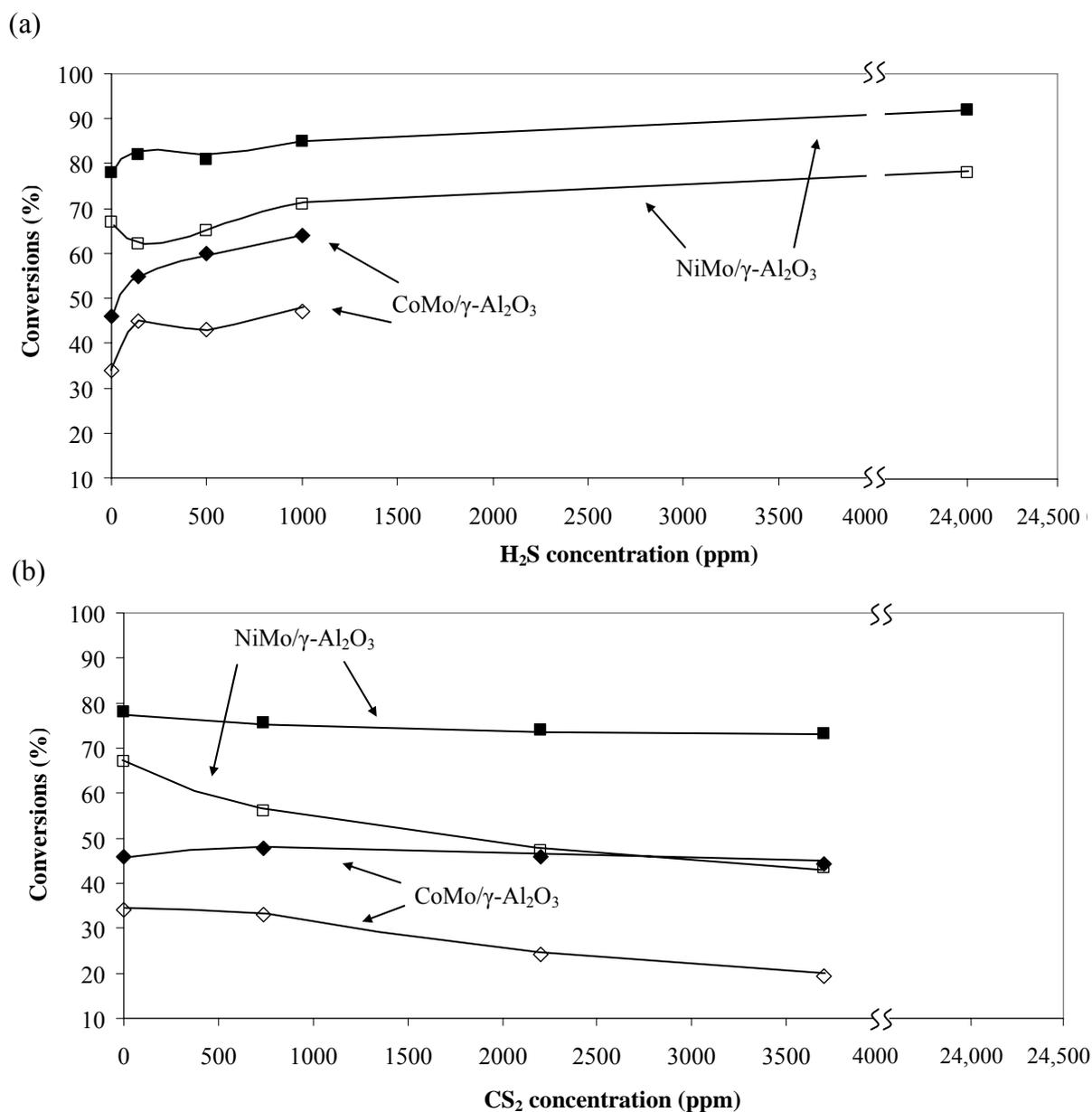


Figure 3.6. Effect of (a) H₂S and (b) CS₂ on total (■, ◆) and HDO (□, ◇) conversions of methyl heptanoate on sulphided catalysts in the gas phase at 250 °C under 1.5 MPa pressure.

On both catalysts, the addition of CS₂ up to 3700 ppm had no clear effect on total conversion of methyl heptanoate, and HDO conversion decreased as a function of CS₂ concentration (Figure 3.6b). Evidently, the addition of CS₂ inhibited the HDO of the

aliphatic ester on the sulphided catalysts. The hydrogenation of CS_2 forms H_2S and CH_4 under the reactions conditions, and therefore the additions of CS_2 and H_2S would be expected to produce similar effects. However, significantly increased carbon content with the addition of CS_2 compared to the addition of H_2S likely caused the inhibiting effect since enhancing acidity in the presence of a sulphiding agent increases the amount of coke formation [29].

The yield of C_6 hydrocarbons formed in the reactions of methyl and ethyl heptanoate increased with the addition of H_2S , as seen in Figure 3.7. The yield of C_7 hydrocarbons was practically unaffected by the presence of H_2S in the reactions of the esters and the carboxylic acid (Figure 3.7). As a result, the addition of H_2S shifted the main products to hexane and hexenes on the NiMo and CoMo catalysts, respectively. These results revealed promotion of the routes, in particular, to C_6 hydrocarbons. The enhanced conversions upon addition of H_2S in the experiments with heptanol clearly indicated promotion of the dehydration reaction. It is probable that, in the reactions of the esters, the routes to heptanol were suppressed by H_2S , and the formation of C_7 hydrocarbons was limited by the concentration effect of heptanol.

The additions of H_2S and CS_2 reduced the molar ratios of saturated to unsaturated hydrocarbons on the NiMo catalyst (Paper IV, Table 4), revealing the inhibition of the hydrogenation reactions. On the CoMo catalyst, however, effect of the sulphiding agent on the hydrogenation reactions was not apparent as the molar ratios did not change noticeably. In several studies, the addition of a sulphiding agent to HDO, HDS and HDN feeds were shown to suppress the hydrogenation reactions on sulphided NiMo/ Al_2O_3 catalysts, and to scarcely affect them on sulphided CoMo/ Al_2O_3 catalysts [32,35,40,43,61,65,66]. Thus, the effect of sulphiding agents on the hydrogenation reactions observed in this work resembled those reported in literature. The decrease in the hydrogenation activity likely affected also the other steps where hydrogen is involved, such as formation of heptanol (Figure 3.2). As a result, the formation rate of heptanol can decrease with the addition of H_2S , resulting in the concentration effect mentioned above.

From the industrial point of view, an important observation for the effect of sulphiding agents on the product distribution is that, according to Figure 3.2, the addition of a

sulphiding agent reduces the carbon efficiency as a result of increasing formation of carbon oxides. On the positive side, the shift in main products decreases hydrogen consumption.

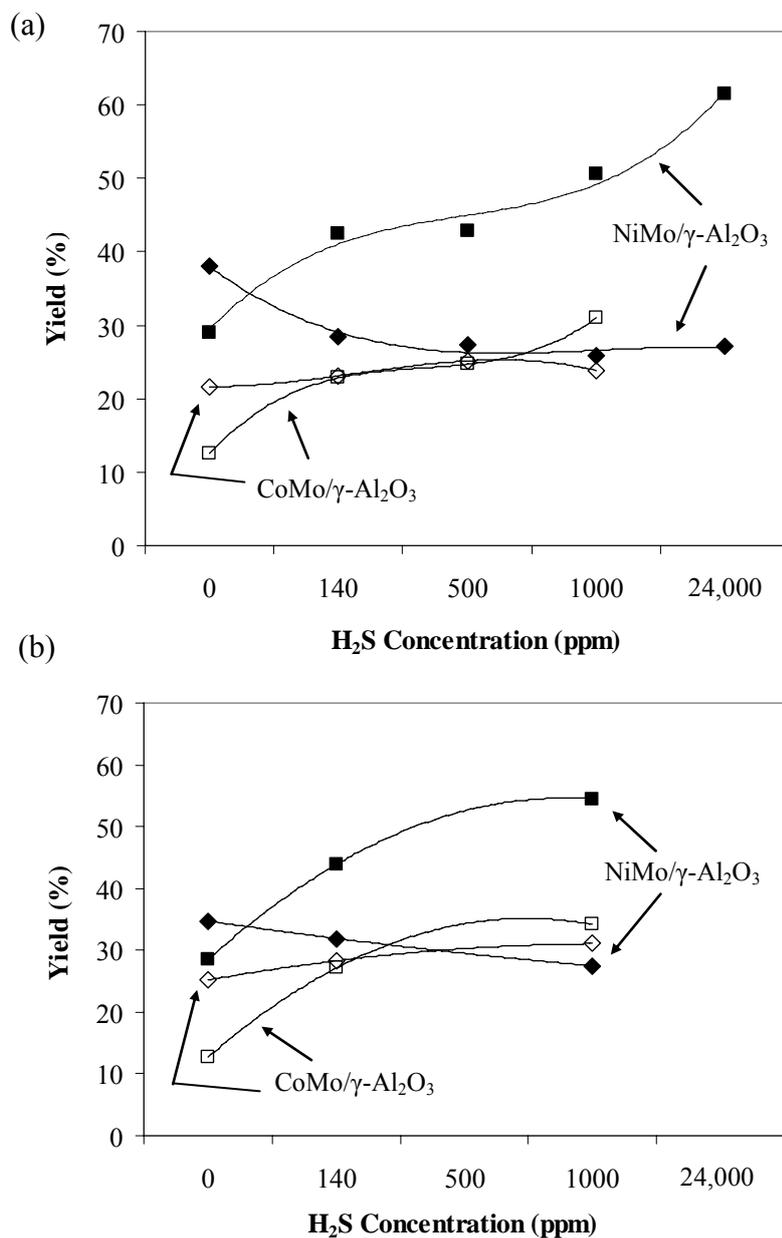


Figure 3.7. Effect of H₂S on the yield of C₇ (◆, ◇) and C₆ (■, □) hydrocarbons formed in the reactions of (a) methyl heptanoate and (b) ethyl heptanoate on sulphided catalysts in the gas phase at 250 °C under 1.5 MPa pressure (Paper IV).

Chapter 4

Reactions of Aromatic Oxygenates

Phenolic compounds are present in abundance in wood-based bio-oils. The HDO of aromatic compounds was studied with phenol as the model in the absence and presence of H_2S . After a description of the reaction products and scheme in section 4.1, the reactivity of phenol and the effect of H_2S on the HDO of phenol are discussed in section 4.2.

4.1 Reactions of phenol

Benzene, cyclohexane and cyclohexene were hydrocarbons found in the liquid samples from both flow and batch reactor studies using phenol as the reactant. In addition, cyclohexanone, diphenyl ether and, in the presence of H_2S , cyclohexanethiol were detected in trace amounts. The concentration profiles of hydrocarbons (Figure 4.1) showed that aromatic and alicyclic hydrocarbons were formed in two parallel reactions where benzene and cyclohexane were the end products, as described in the literature [32,42,43,67].

In some studies, formation of cyclohexanol via hydrogenation of the aromatic ring of phenols has been reported [32,41]. Cyclohexanol was not detected in this work, but formation of cyclohexanone suggested hydrogenation of the aromatic ring prior to the formation of hydrocarbons. However, because of the $\text{C}=\text{O}$ π -bond in the cyclohexanone molecule, a hydrogenation step before the elimination of the oxygen atom, and hence formation of an intermediate cyclohexanol could be expected. In the experiments with cyclohexanone and cyclohexanol as the model compounds, formation of only cyclohexane

and cyclohexene revealed that these alicyclic oxygenates were possible intermediates in the formation of alicyclic hydrocarbons but not in the formation of benzene. The conversion of cyclohexanone and cyclohexanol was complete in the flow reactor studies, indicating their high reactivity on the sulphided catalysts. Concentration profiles of cyclohexane and cyclohexene in the batch reactor studies (Paper V, Figure 2) revealed a consecutive formation of cyclohexene and cyclohexane.

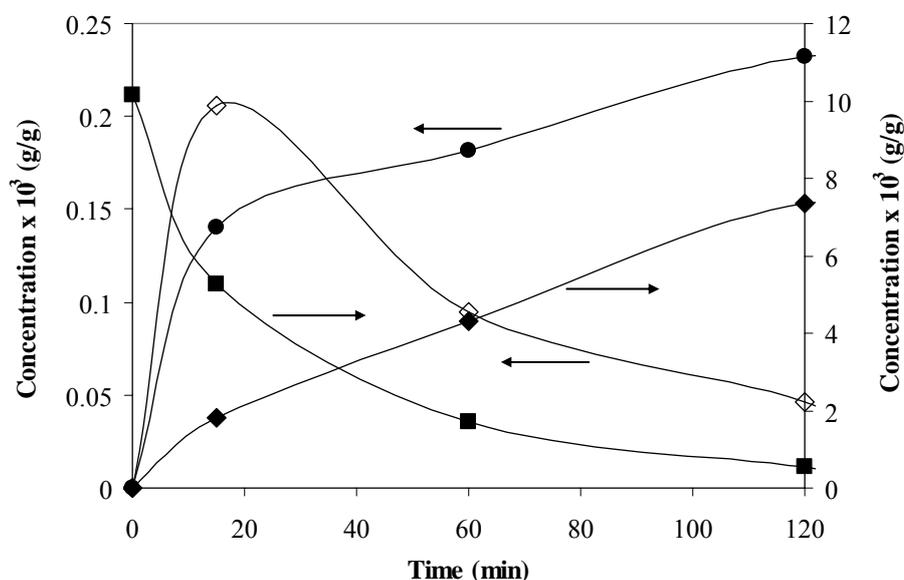


Figure 4.1. Concentration profiles of phenol (■), benzene (●), cyclohexane (◆) and cyclohexene (◇) in the absence of H_2S at 250 °C under 7.5 MPa pressure in the batch reactor (catalyst: sulphided NiMo/ γ - Al_2O_3 , Paper V).

Reactions of benzene were studied on both catalysts in the batch reactor. Formation of cyclohexane and cyclohexene in trace amounts was detected, but the conversion to hydrocarbons was less than 1.5% at the end of a 60-min run. As a result, it was concluded that hydrogenation of benzene was negligible under the studied conditions.

A reaction scheme for the HDO of phenol on sulphided catalysts was proposed on the basis of these findings (Figure 4.2). The reaction scheme and the formation of cyclohexanethiol will be discussed further in the following section.

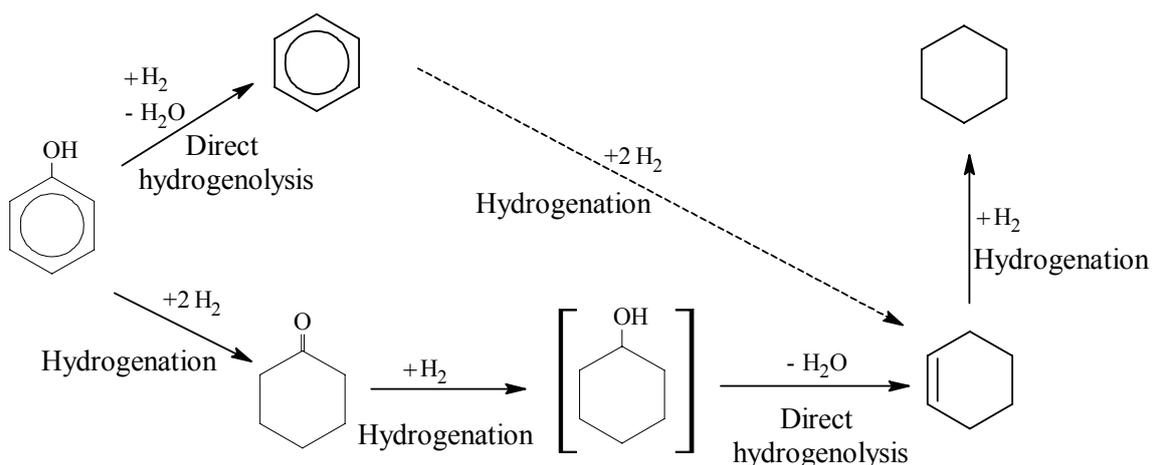


Figure 4.2. HDO reaction scheme of phenol on the sulphided catalysts (Paper V).

4.2 Effect of hydrogen sulphide on catalyst activities and product distributions

Cyclohexane on the NiMo catalyst and benzene on the CoMo catalyst were formed as the main HDO products of phenol, revealing that the route to alicyclic hydrocarbons was more important than the route to aromatic product on the NiMo catalyst, while the situation was the reverse on the CoMo catalyst. The formation of mainly cyclohexane on the NiMo catalyst is in good agreement with the high hydrogenation activity of the catalyst [22,30]. The yield of cyclohexene on both catalysts never exceeded 2%.

The HDO conversion of phenol in the gas phase experiments in the absence of a sulphiding agent was 19% on the NiMo catalyst and 28% on the CoMo catalyst, and it decreased as a function of the concentration of H_2S in the feed (Paper V, Figure. 3). Likewise, the yields of aromatic and aliphatic hydrocarbons dropped, as seen in Figure 4.3. Clearly, H_2S inhibited the HDO of phenol, and the inhibition occurred in both routes to aromatic and alicyclic hydrocarbons. The inhibition on the NiMo catalyst was similar for both routes as the molar ratios of aromatic to alicyclic hydrocarbons did not change significantly with the addition of a sulphiding agent. On the CoMo catalyst, however, the route to benzene was suppressed more than the route to alicyclic hydrocarbons as the molar ratio of aromatic to

alicyclic hydrocarbons decreased notably with increasing concentration of sulphiding agent.

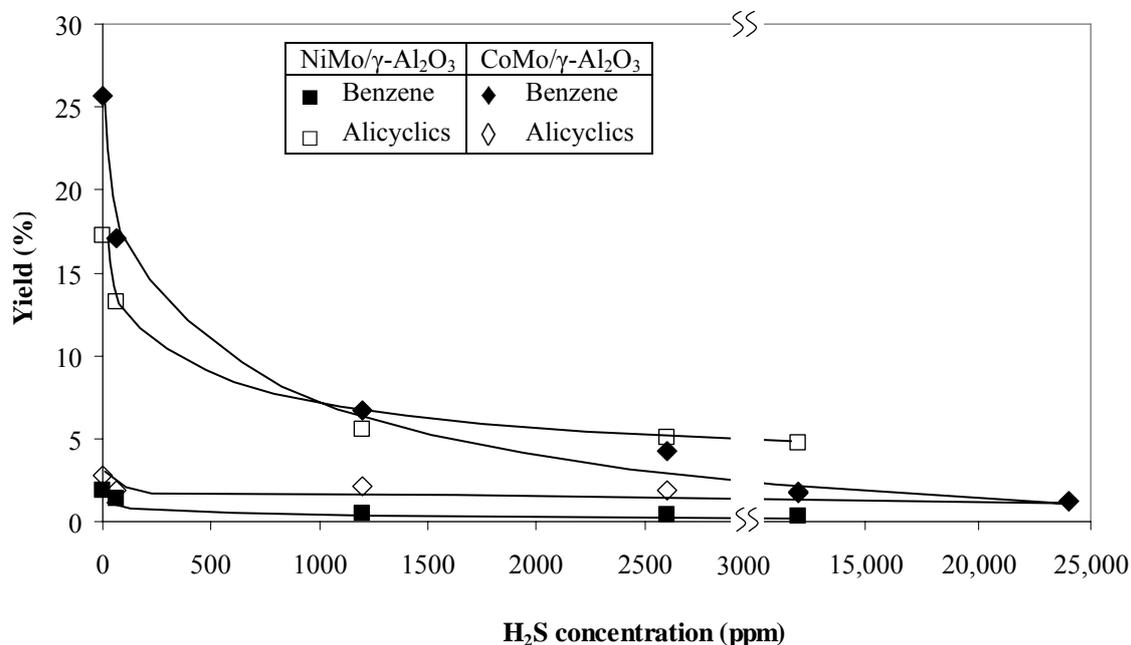


Figure 4.3. Effect of H₂S on the yield of benzene and alicyclic hydrocarbons formed in the reactions of phenol on sulphided catalysts in the gas phase at 250 °C under 1.5 MPa pressure (Paper V).

In principle, rupture of the C-O σ -bond can occur both by an acid-catalysed dehydration reaction and by a direct hydrogenolysis reaction. However, the dehydration reaction is unlikely since neither α - nor β -carbon atom is saturated in the phenol molecule. Therefore, the formation of benzene was explained in terms of the direct hydrogenolysis reaction (Figure 4.2). Accordingly, the sulphur anion vacancies (CUS) were proposed to be the catalytic centres for the direct hydrogenolysis reaction of phenol, and the inhibition by H₂S was attributed to the competitive adsorption of phenol and H₂S on the catalysts.

Since both the α - and β -carbon atoms in the cyclohexanol molecule are saturated, alicyclic hydrocarbons can be formed both by the dehydration reaction and by the direct hydrogenolysis reaction. The dehydration reaction, which can occur by E₁ and E₂ mechanisms, and the role of S_N1 and S_N2 nucleophilic substitution reactions in the

formation of cyclohexanethiol were explained in Scheme 2 in Paper V. Additional experiments with cyclohexanol in the batch reactor showed that the addition of 3800 ppm sulphiding agent reduced the HDO conversion about 7 percentage units at end of a 60-min run. Accordingly, the direct hydrogenolysis reaction was concluded to be the major reaction for the formation of alicyclic hydrocarbons, and the inhibition by the sulphiding agent was attributed to the competitive adsorption. This conclusion further suggested the role of the same catalytic sites, i.e. sulphur anion vacancies, in the formation of aromatic and alicyclic hydrocarbons.

Looking at the molar ratios of cyclohexane to cyclohexene (Figure 4.4), the addition of H₂S suppressed the hydrogenation reactions on the NiMo catalyst, and did not affect them on the CoMo catalyst since the molar ratios decreased on the former catalyst and did not alter on the latter. Similar results were obtained in the experiment with cyclohexanol.

The sulphur contents of the catalysts were nearly maintained in the absence and presence of H₂S. The carbon contents increased up to 5.0-6.0 wt%, but no correlation was found between the increases and the concentration of sulphiding agent.

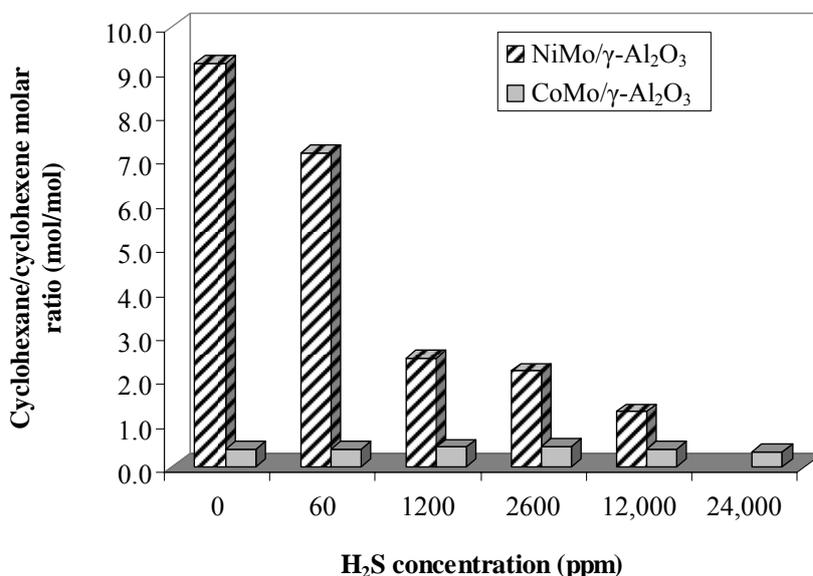


Figure 4.4. Effect of H₂S on the molar ratio of cyclohexane to cyclohexene formed on sulphided catalysts at 250 °C under 1.5 MPa pressure in the flow reactor (Paper V).

Chapter 5

Hydrodeoxygenation of Aliphatic versus Aromatic Oxygenates

Esters, alcohol and carboxylic acid as the aliphatic model compounds and phenol as the aromatic model compound demonstrate a clear difference in HDO reactivity on sulphided catalysts. Experiments with the non-sulphided catalysts showed that the HDO of aliphatic oxygenates, unlike the HDO of phenol, proceeds to some extent on these catalysts. Comparison of the HDO conversions of aliphatic oxygenates and phenol revealed that, under similar reaction conditions, the aliphatic oxygenates were more reactive than phenol in both the absence and presence of a sulphiding agent.

The promoting effect of H₂S on the HDO of the ester and the inhibiting effect on the HDO of phenol are explicitly seen in Figure 5.1. Since sulphur anion vacancies on the catalyst surface were proposed to play a role both in the HDO of aliphatic oxygenates and in the HDO of phenol, the effects of sulphiding agent on the HDO would be expected to be the same. However, the role of acid-catalysed reactions (hydrolysis, dehydration, esterification, elimination and nucleophilic substitution) in the HDO of aliphatic oxygenates indicated the significance of the acidic properties of the catalysts in the reactions of aliphatic oxygenates. The addition of sulphiding agent promoted the acid-catalysed reactions as a result of increased Brønsted acidity. The direct hydrogenolysis reaction taking place in the HDO of phenol, on the other hand, was not directly related to the acidity of the catalysts but rather to the availability of active sites and hydrogen. The

addition of a sulphiding agent suppressed the direct hydrogenolysis reactions because of competitive adsorption. Thus, the opposite effects of H₂S on the HDO of phenol and aliphatic oxygenates were attributed to the different reaction mechanisms. This difference is possibly related to the different molecular and electron structures of aliphatic and aromatic oxygenates.

The addition of sulphiding agent affected the hydrogenation reactions occurring in the HDO of model aliphatic and aromatic oxygenates similarly. Accordingly, same catalytic sites were concluded to be responsible for the hydrogenation reactions in the HDO of aliphatic and aromatic oxygenates.

Formation of sulphur-containing compounds in the HDO of aliphatic oxygenates even in the absence of a sulphiding agent in the feed suggested a role of reactive sulphur species on the catalyst surface in the formation of sulphur-containing compounds. The situation was, however, not the same for HDO of phenol, and a sulphur-containing compound was detected only when a sulphiding agent was added to the reactor.

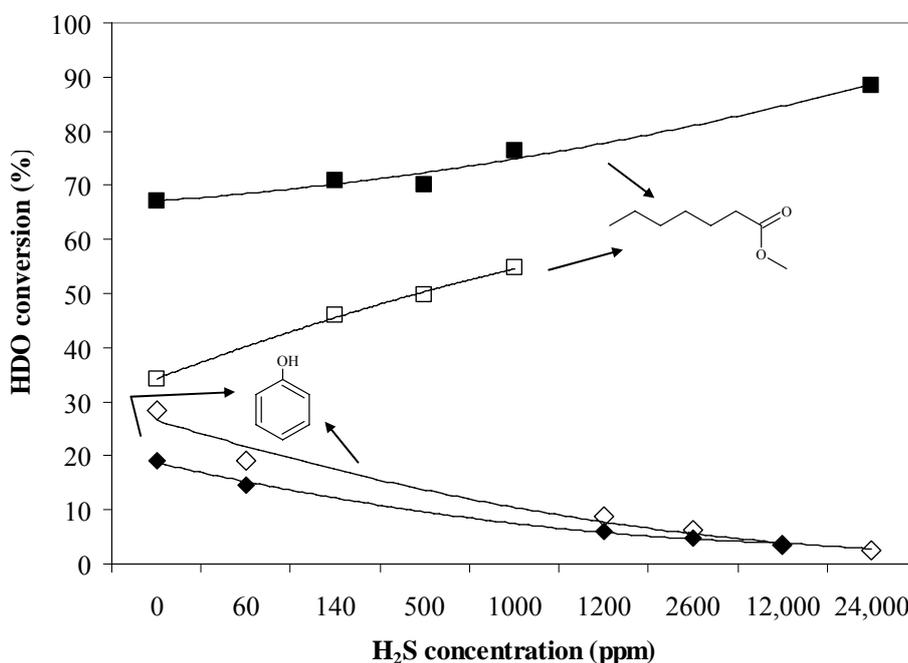


Figure 5.1. The effect of H₂S concentration on the HDO conversion of methyl heptanoate and phenol on sulphided NiMo/γ-Al₂O₃ (■, ◆) and CoMo/γ-Al₂O₃ (□, ◇) catalysts in the gas phase at 250 °C under 1.5 MPa pressure.

Chapter 6

Concluding Remarks and Outlook

Liquid biofuels produced from renewable resources contain various aliphatic and aromatic oxygenates. Biofuels from vegetable oils and animal fats contains aliphatic oxygenates and those from wood mainly aromatic oxygenates. The high oxygen content restricts the utilisation of biofuels in the transport sector and, therefore, it needs to be decreased. Hydrodeoxygenation (HDO) can provide a method for the upgrading of biofuels. In this work, HDO of aliphatic and aromatic oxygenates was studied on sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts. The effects of water and H₂S on the reactions of aliphatic oxygenates and the effect of H₂S on the reactions of aromatic oxygenates were investigated. The effect of H₂S on the HDO of aliphatic oxygenates was studied by adding H₂S as such and in the form of CS₂.

The HDO of aliphatic oxygenates produced saturated and unsaturated hydrocarbons by removal of oxygen in the form of water, CO₂ and CO. Oxygen- and sulphur-containing compounds were formed as intermediates in the reactions. The formation of sulphur-containing compounds led to desulphurisation of the catalysts. Hydrogenation reactions and acid-catalysed reactions (hydrolysis, dehydration, esterification, elimination and nucleophilic substitution) played a role in the HDO of aliphatic oxygenates. Thus, catalyst acidity was an important factor affecting the reactions of aliphatic oxygenates on sulphided catalysts. The HDO of phenol as the aromatic model compound, on the other hand, produced aromatic and alicyclic hydrocarbons in two parallel reactions, direct hydrogenolysis reaction and hydrogenation reaction followed by direct hydrogenolysis

reaction. Alicyclic hydrocarbons were formed from intermediate cyclic oxygenates (cyclohexanone and cyclohexanol).

Water inhibited the HDO of aliphatic oxygenates. In contrast, the sulphiding agent H_2S had a promoting effect. The addition of H_2S effectively compensated the inhibition by water, but did not prevent the catalyst deactivation. The effect of H_2S was attributed to promotion of the acid-catalysed reactions due to increased catalyst acidity. The addition of H_2S changed the product distribution in such a way that carbon efficiency and hydrogen consumption decreased. When CS_2 was added as the sulphiding agent, the HDO of aliphatic oxygenates was inhibited due to significant carbon deposition.

On both catalysts, the addition of H_2S suppressed the direct hydrogenolysis reaction, and hence it inhibited the HDO of phenol. The inhibition was explained by competitive adsorption of H_2S and phenol. As a result, the opposite effect of H_2S on the HDO of aliphatic and aromatic oxygenates was attributed to the difference in the reaction mechanisms (dehydration, hydrolysis, elimination and direct hydrogenolysis reactions). The effect of water and H_2S on the hydrogenation reactions was similar in the HDO of aliphatic and aromatic oxygenates, however. These reactions were inhibited on the NiMo catalyst, and they were not affected on the CoMo catalyst in the HDO of both aliphatic and aromatic oxygenates.

Aliphatic oxygenates were hydrodeoxygenated even on the non-sulphided catalysts. The activity of the catalysts was highest for the sulphided form, however, but these catalysts deactivated due to desulphurisation and coke formation. The results showed that aliphatic oxygenates were more reactive on sulphided catalysts than the aromatic oxygenate phenol. Comparison of the catalysts showed that the NiMo catalyst has a better HDO (especially for aliphatic oxygenates) and hydrogenation activity than the CoMo catalyst. The hydrogen consumption, therefore, increased with the use of NiMo catalyst, as expected.

This work demonstrates that the composition of biofuels affects the overall HDO performance of sulphided catalyst. The effect of sulphiding agent added to the HDO feed to maintain activity and stability of the catalyst can vary greatly between the HDO of wood-based biofuels, which contain mainly aromatic oxygenates, and the HDO of biofuels from vegetable oils and animal fats, which contain aliphatic oxygenates. Although the

applicability of the results of this work in developing a large-scale process for the production of liquid biofuels is limited due to use of the model compounds, this work provides a reference for future research, focusing on the HDO of mixtures of aliphatic and aromatic oxygenates and their kinetic analysis. Vegetable oils and animal fats typically contain longer carbon chains (14-22 carbon atoms) than the model aliphatic oxygenates studied in this work. Therefore, the use of aliphatic oxygenates with longer carbon chain in the mixture in order to mimic real biofuels may be considered. In that case, operation in a trickle phase in the flow reactor system is probable.

Since the sulphided catalysts are active in the HDO reactions, an interesting possibility would be operation of existing refinery HDS processes as HDS-HDO cycles by changing the feed stream or as simultaneous HDS and HDO. A few studies regarding HDS-HDO cycles and simultaneous HDS and HDO have been carried out with molecules such as anisole, phenol, mercaptobenzene and benzothiophene in our laboratory [66,68,69]. Recently, a simultaneous conversion of vegetable oils and mineral oils in an existing hydrotreating unit has been successfully operated and the process was patented by the Brazilian oil company Petrobras [70]. However, specifications of the diesel product are not suitable for cold-climate regions like The Nordic Countries and Canada.

Since the sulphur content of biofuels is low, addition of a sulphiding agent to the feed is typically needed, as mentioned before. However, future work may be extended to the application of metal catalysts in biofuel conversion, in order to eliminate the use of sulphur compounds totally. Certainly, a biofuel upgrading process in which no sulphur is involved would be economically and environmentally favourable.

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