FROM BIOMASS TO FUELS: HYDROTREATING OF OXYGEN-CONTAINING FEEDS ON A CoMo/Al$_2$O$_3$ HYDRODESULFURIZATION CATALYST

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ABSTRACT

Biomass is a renewable alternative to fossil raw materials in the production of liquid fuels and chemicals. Liquefied biomass contains an abundance of oxygen-containing molecules that need to be removed to improve the stability of the liquids. A hydrotreating process, hydrodeoxygenation (HDO), is used for the purpose. Hydrodeoxygenation is similar to the hydrodesulfurization (HDS) process used in oil refining, relying upon a presulfided $CoMo/\gamma\text{-}Al_2O_3$ catalyst. The stability of the sulfided catalyst is critical in HDO because biocrudes usually do not contain the sulfur compounds needed to maintain the sulfidation of the catalyst.

The aim of this work was to examine the role of sulfur in maintaining the activity of the HDO catalyst. Sulfur was introduced as an organic sulfur-containing co-reactant or as a sulfur substituent in an oxygen-containing reactant molecule as a way of simulating mixed feeds composed of biocrudes and conventional crudes, or it was introduced as a low molecular weight sulfiding agent. In addition, the stability of the sulfided catalyst against changes in the feed composition was studied to find out whether the activity of the catalyst could be maintained by carrying out HDO alternately with HDS.

Simultaneous HDO and HDS was studied in a batch reactor with model compounds having a sulfur-containing (mercapto or methylmercapto) and an oxygen-containing (hydroxyl or methoxy) substituent in the same molecule, and with binary mixtures of mono-substituted benzene compounds. In both cases, the reactions of the oxygen-containing substituents were strongly suppressed as long as a sulfur-containing functionality was present. HDS reactions of mercapto and methylmercapto groups were either enhanced or retarded in the presence of oxygen-containing functionality. HDS was enhanced when the oxygen-containing substituent was located in *para*-position to the sulfur substituent thereby increasing the electronegativity of the sulfur atom and thus facilitating the adsorption of the reactant on the active site of the catalyst. Otherwise, the HDS rate declined due to strong competitive adsorption of the oxygen-containing compounds on the active sites of the catalyst, and due to the formation of less reactive

sulfur compounds via methyl transfer from the methoxy groups to sulfur. In conclusion, simultaneous hydrotreating of sulfur- and oxygen-containing feeds leads to strong suppression of oxygen removal reactions and usually also to a decrease in the efficiency of sulfur removal.

The effect of low molecular weight sulfiding agents, H_2S and CS_2, on HDO of phenol and anisole was studied first in a batch and then in a flow reactor to see whether the addition of sulfiding agents might improve the stability of the presulfided catalyst without decreasing the rate and without affecting the selectivity of HDO. The HDO rate of phenol decreased noticeably in the presence of CS_2 in the batch reactor, and the selectivities of the HDO reaction paths were changed: the hydrogenation–hydrogenolysis route was less sensitive to the sulfur compound than was the C_{Arom}–O hydrogenolysis path. At higher concentrations of the sulfiding agent, also the hydrogenation route became inhibited. With anisole, there was an increase in the rate of demethylation to phenol, but oxygen removal was virtually unaffected. In the flow reactor studies, the formation of hydrogenated HDO products of phenol remained constant up to the highest concentration of H_2S in the feed, but a dramatic decrease in the yield of the aromatic reaction product occurred already at low concentrations of H_2S. Selective inhibition of one of the HDO paths confirmed the presence of at least two kinds of active sites on the catalyst. This means that addition of an inhibitor can be used to adjust the product distribution of HDO in process scale. However, the presulfided catalyst deactivated with time on stream also in the presence of sulfiding agents.

Finally, the stability of the presulfided catalyst against changes in the feed composition was studied in a flow reactor. HDO of phenol and HDS of benzothiophene were carried out alternately in periods of four to eight hours. In this way, the deleterious effect of the competition of HDO and HDS was almost totally avoided and the stability of the catalyst during HDO was improved. The lengths of the HDO and HDS periods now need to be optimized.

PREFACE

LIST OF PUBLICATIONS

The thesis is based on the following publications, which are referred to in the text by the corresponding Roman numerals (Appendices I–VI):

I.   Viljava, T.-R. and Krause, A.O.I., Hydrogenolysis reactions in a batch reactor. Effect of mass balance inaccuracies on the kinetic parameters, *Appl. Catal. A: General*, 135 (1996), pp. 317-328.

II.   Viljava, T.-R. and Krause, A.O.I., Hydrotreating of compounds containing both oxygen and sulfur: Effect of *para*-hydroxyl substituent on the reactions of mercapto and methylmercapto groups, *Appl. Catal. A: General*, 145 (1996), pp. 237-251.

III.   Viljava, T.-R. and Krause, A.O.I., Hydrotreating of compounds and mixtures of compounds having mercapto and hydroxyl groups, *Stud. Surf. Sci. Catal.*, 106 (1997), pp. 343-352.

IV.   Viljava, T.-R., Saari, E.R.M. and Krause, A.O.I., Simultaneous hydrodesulfurization and hydrodeoxygenation: Interactions between mercapto and methoxy groups present in the same or in separate molecules, *Appl. Catal. A: General*, 209 (2001), pp. 33-43.

V.   Viljava, T.-R., Komulainen, S., Selvam, T. and Krause, A.O.I., Stability of CoMo/Al$_2$O$_3$ catalysts: Effect of HDO cycles on HDS, *Stud. Surf. Sci. Catal.*, 127 (1999), pp. 145-152.

VI.   Viljava, T.-R., Komulainen, S. and Krause, A.O.I., Effect of H$_2$S on the stability of CoMo/Al$_2$O$_3$ catalysts during hydrodeoxygenation, *Catal. Today*, 60 (2000), pp. 83-92.

The author's contribution in the appended publications is as follows:

I.   The author drew up the research plan, carried out most of the experimental work, interpreted the results and wrote the manuscript.

II.   The author drew up the research plan, carried out most of the experimental work, interpreted the results and wrote the manuscript.

III.   The author drew up the research plan, carried out most of the experimental work, interpreted the results and wrote the manuscript.

IV.   The author drew up the research plan, supervised and participated in the experimental work, interpreted most of the results and wrote the manuscript.

V.   The author drew up the research plan and supervised the experimental work. She participated in the interpretation of the results and wrote the manuscript.

VI.   The author drew up the research plan together with the co-authors and supervised the experimental work. She participated in the interpretation of the results and in writing the manuscript.

ABBREVIATIONS

HDS	Hydrodesulfurization
HDO	Hydrodeoxygenation
HDN	Hydrodenitrogenation
C_{Arom}	Aromatic carbon atom
C_{Aliph}	Aliphatic carbon atom
S_{Arom}	Aromatic sulfur atom
S_{Aliph}	Aliphatic sulfur atom

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1 INTRODUCTION

Biomass has traditionally been used in combustion to produce heat and power. The production of liquid fuels and chemicals is a possibility worth considering for countries having no fossil raw material resources. Biomass is available almost everywhere and its price does not suffer from market fluctuations. Biomass also has clear advantages from the environmental point of view. Since it is renewable, using it would not increase the level of carbon dioxide in the atmosphere. In addition, conversion of waste biomass to liquid fuels and chemicals would reduce the volumes of agricultural and municipal wastes needing to be landfilled.

Production of liquid fuels and chemicals from solid biomass can feasibly be carried out through two routes: (1) via direct liquefaction of biomass to "biocrude" followed by upgrading into hydrocarbons, and (2) via indirect liquefaction processes in which biomass is first converted to H_2 and CO, and the gases are synthesised into liquid products (see Figure 1) [1-3]. The direct liquefaction of biomass followed by upgrading and refining is regarded as the more promising approach although indirect liquefaction processes such as the MTG process (Mobil methanol to gasoline process) and the SMDS process (Shell middle distillate synthesis process), are reported to give high-quality products [2]. Other possibilities exist with some special types of biomass; for example, biodiesel can be produced from mechanically separated vegetable oils through esterification and transesterification processes [4], and hydrolysed biomass can be fermented to ethanol [2]. However, the use of fuel alcohols in place of gasoline requires modification of existing engines and delivery systems.

CONVERSION TECHNOLOGY:

Liquefaction to biocrudes:
1. High pressure liquefaction
2. Pyrolysis

Gasification to CO + H$_2$

Enzyme/acid hydrolysis

BIOMASS:

- Wood
- Wood wastes
- Peat
- Grasses
- Agricultural wastes
- Municipal solid wastes

PROCESS:

Upgrading:
1. Hydrotreating
2. Zeolite process

Synthesis of fuels and chemicals:
1. Methanol synthesis
2. Fischer-Tropsch synthesis
3. MTG (methanol to gasoline) process
4. SMDS (Shell middle distillate synthesis

Fermentation

PRODUCT:

- Gasoline
- Diesel
- Fuel oil
- Chemicals

- Methanol
- Liquid fuels
- Chemicals

- Ethanol

Figure 1. Routes from biomass to fuels and chemicals.

1.1 Synthetic crudes from biomass

Biocrude—also known as bio-oil—can be produced from biomass either by liquefaction under high pressure or by pyrolysis at near-ambient pressure [1,2,5-12]. Wood is commonly used as a feedstock in liquefaction: processing residues, forest residues, trees from thinning and the produce from short-rotation energy forestry plantations have all been utilised [7]. Wood consists of cellulose, hemicellulose and lignin, and the aromatic structure of lignin makes it an important source of useful chemicals [1]. Peat and agricultural and municipal solid wastes are alternative resources [1,2,6,8-12]. High-pressure liquefaction of biomass gives lower yields of biocrude at higher cost than does liquefaction via pyrolysis processes, but the product quality is better from the former, i.e. the oxygen and the water content of the product are lower [1,9-11,13]. Recent studies on biomass liquefaction have focused on pyrolysis processes.

Biomass-based oils are very different from crude oils from petroleum sources; the sulfur content of biocrudes is negligible, while they are rich in oxygen-containing molecules (see Table 1). The type of the oxygen compounds depends on the raw material and on the conditions of the liquefaction process [1,6,12,14]. Carboxyl, carbonyl, hydroxyl and methoxy functionalities are typically present [1,11,14-16]. The oxygen compounds are responsible for some deleterious properties of the crudes: high viscosity, non-volatility, corrosiveness, immiscibility with fossil fuels, thermal instability and tendency to polymerize under exposure to air [1,6-8,12-15]. Thus upgrading of biocrudes means removal of oxygen. Deoxygenation of biocrudes can be carried out by a process based on a zeolite catalyst or by a hydrotreating process, hydrodeoxygenation (HDO), similar to the hydrodesulfurization (HDS) process that is an essential part of oil refining [6]. No reducing gases are used in the zeolite process, and oxygen is released as carbon dioxide and water. The product is highly aromatic and of high value. However, the process suffers from poor yield of hydrocarbons due to bypassing of the larger molecules of the biocrude and to the catalyst deactivation caused by coking [6].

1.2 Hydrodeoxygenation

Because of the low oxygen content of conventional crudes, HDO has been much less thoroughly studied than HDS. In addition to biocrudes, HDO is of importance in the utilisation of coal and oil shale, although the oxygen content of crudes based on these raw materials is much lower than that of biocrudes (see Table 1). As an upgrading process, HDO of bio-oils typically comprises two stages [1,6-7,13]. The first, so-called stabilisation stage is carried out at lower reaction temperatures in order to avoid polymerization of the oxygen-containing compounds and coking of the catalyst during the following deoxygenation step. At the second stage, under more severe reaction conditions, oxygen removal is efficient and large amounts of hydrogen are consumed. The first stage—also called mild hydrotreating—can be applied at lower cost to produce partially deoxygenated fuels suitable for the generation of electricity and heat [17-18]. Partial hydrotreating of biocrudes can also be applied in the production of some chemicals [6].

Table 1. Hetero atom contents of different feeds [13].

	Conventional crude	Coal-derived naphtha	Oil shale crude	Bio-oils	
				Liquefied	Pyrolysed
Hetero atom, wt-%					
Sulfur	1.8	0.1	0.5	<0.1	<0.1
Nitrogen	0.1	0.5	1.4	<0.1	<0.1
Oxygen	0.1	4.7	1.2	16.6	46.9
Total	2.0	5.3	3.1	<16.8	<47.1

Conventional HDS catalysts—sulfided molybdenum and cobalt or nickel on alumina support (CoMo/γ-Al$_2$O$_3$ or NiMo/γ-Al$_2$O$_3$)—have typically been used in HDO of biocrudes [1,5-7,9,13-16,19]. In recent years, experimental work has also been directed towards catalyst development, and neutral support materials such as carbon have been studied in the HDO of model feeds in the attempt to avoid the coke formation caused by the activity of the acidic γ-Al$_2$O$_3$ support [15,20-26].

Most HDO studies reported in the literature have been carried out using model compounds and mixtures of model compounds rather than real biocrudes. The experimental work has been extensively summarised in the recent review by Edward Furimsky [13]. Most attention within the HDO field has been paid to phenols and furans because of their low reactivity in HDO. Two routes in the oxygen removal reactions of phenols have been observed: (1) the aromatic ring of the oxygen-containing molecule is either retained and the bond between the aromatic carbon and the oxygen atom hydrogenolysed (C$_{Arom}$–O hydrogenolysis route), or (2) the aromatic ring is hydrogenated before cleavage of the carbon–oxygen bond (hydrogenation–hydrogenolysis route) [13]. In general, HDO of an oxygen-containing compound proceeds at a lower rate than the HDS of a sulfur-containing compound of similar structure. In addition, the HDO

reactions are self-inhibited by the oxygen-compound and inhibited by oxygen-containing intermediates and products, as well as by the sulfur-containing and nitrogen-containing compounds [13,27].

1.3 Sulfided CoMo/Al$_2$O$_3$ catalyst

Coordinatively unsaturated sites (CUS), or sulfur anion vacancies, which are located at the edges of MoS$_2$ slabs supported on γ-Al$_2$O$_3$, are believed to be the sites for catalytic hydrotreating reactions [13,28-29]. Double and even multiple vacancy centres may be present. The presence of Co (or Ni) promotor does not appreciably increase the number of vacancies, but the activity of the vacancies is considerably increased. The presence of so-called Co-Mo-S structures on the catalysts has been suggested and, recently, single-layer Co-Mo-S nanostructures have been synthesised and their structure studied by scanning tunnelling microscopy [30]. During HDO, the oxygen-containing compounds and the water formed in HDO reactions may change the structure of the sulfide catalyst, and in most studies sulfur-donating species have been added to the sulfur-free HDO feed to compensate for desulfurization of the catalyst.

The presence of two separate active sites one for hydrogenolysis and the other for hydrogenation reactions, often has been indicated on the sulfided catalyst [13]. It has been suggested that the oxygen-containing reactant is adsorbed on the hydrogenolysis site via σ-bond to the oxygen atom and on the hydrogenation site via π-bond to the aromatic ring. At least one group [31-33] has proposed an interconversion of these sites with changes in the H$_2$-H$_2$S ratio during HDO. At low H$_2$S concentrations, the hydrogenation route is reported to be promoted to some extent owing to site interconversion. At higher H$_2$S concentrations, both types of active site are deactivated. In addition to these active sites, the sulfhydryl groups of the catalyst and the acidic sites of the γ-Al$_2$O$_3$ support may play a role in hydrotreating reactions [13,29].

1.4 Scope of the work

Studies reported in the literature suggest that the technology used for HDS also could be applied for HDO of biocrudes. Even though prices still favour conventional oil refining, environmental aspects and limited petroleum resources support an eventual switch to renewable raw materials. During the transitional stage, it would be tempting to carry out HDO of biocrudes as such, or simultaneously with HDS of conventional crudes, using already existing refinery facilities. However, a great number of questions remain unanswered in regard to HDO, above all those concerning the sulfided catalyst of the HDS process: biocrudes do not contain sulfur, and some sulfur is believed to be needed to maintain the activity of the catalyst during HDO. On the other hand, sulfur-containing compounds have turned out to be inhibitors for HDO, at least to some extent, due to competitive adsorption on the active sites of the catalyst. These contradictory effects of sulfur have not yet been unambiguously distinguished.

There are at least two ways in which the sulfidation level of the presulfided catalyst might be maintained during HDO: one is simultaneous hydrotreating of oxygen- and sulfur-containing feeds, and the other is the addition of low molecular weight sulfiding agents to the HDO feed. Both these approaches were tested. In the case of simultaneous HDS and HDO, it was important to find out to what extent and in what way the competition between the oxygen and sulfur atom removal reactions and the interaction of the atoms affect the efficiency of the operation. With low molecular weight sulfiding agents, different concentrations in the feed were studied in order to find the concentration with minimum inhibition effect. From the practical point of view, it also was important to study the stability of the catalyst against changes in the feed composition. This thesis summarises the findings of research on these subjects.

Simultaneous hydrotreating of oxygen- and sulfur-containing feeds was studied in a batch reactor, and the stability of the catalyst was investigated in a flow reactor. After the suitability of the batch reactor to produce accurate reaction data for determination of the kinetic parameters was confirmed, the parameters were determined for simple HDS and

HDO reactions separately [I]. Simultaneous HDO and HDS was then studied with a variety of model compounds and their mixtures by applying the methods developed in the first part of the work [II-IV]. The study was focused on the rate and the temperature sensitivity of the reaction steps. Finally, study was made of the stability of the presulfided catalyst during HDO: the selectivity and activity of the sulfide catalyst were determined in the absence and presence of sulfiding agents, and some alternative procedures to maintain the degree of sulfidation were tested [V, VI]. In addition, the stability of the catalyst in hydrotreating of sulfur-containing and oxygen-containing feeds alternately was preliminarily tested [V].

2 EXPERIMENTAL

2.1 Catalyst and chemicals

The catalyst was a commercial hydrodesulfurization catalyst, Ketjenfine 742-1.3Q, which contained 4.4 wt.% of CoO and 15 wt.% of MoO_3 on γ-Al_2O_3. The catalyst was crushed and sieved to a fraction of 0.75-1.0 mm for the batch reactor studies [I-IV], calcined under nitrogen and presulfided with CS_2 in n-hexane under hydrogen at 280 °C and 5 MPa. A catalyst fraction of 0.5-0.75 mm was used in the flow reactor. The catalyst was packed between two layers of silicon carbide (1-3 mm) and calcined at 400 °C under nitrogen. It was then used as such in the hydrotreating tests or it was presulfided in situ with 5% H_2S/ H_2 at 400 °C for 4 hours [V, VI]. In earlier work with a flow reactor this presulfidation method was found to give the catalyst sulfur content that corresponds to the calculated sulfur content for proper sulfidation [34].

The chemicals and gases that were used are listed in Table 2. All the chemicals were used as received. *para*-Mercaptophenol [II, III] was stored under an argon atmosphere.

Table 2. Gases and chemicals.

Chemical	Supplier	Purity	Ref.
Gases:			
H_2	Aga	99.999%	I–VI
N_2	Aga	99.999%	I–VI
0.254% H_2S/H_2	Aga	± 3% rel.	VI
5% H_2S/H_2	Aga	4.67±0.23%	V,VI
Sulfur compounds[a]:			
CS_2	Merck	> 99.99%	I–IV, VI
mercaptobenzene (thiophenol)	Merck	> 98%	I–IV
(methylmercapto)benzene (thioanisole)	Merck	> 98%	II
diphenylsulfide	Fluka	> 97%	I
benzothiophene	Fluka	> 97%	V, VI
Oxygen compounds[a]:			
phenol	Carlo Erba	> 99.5%	I–III
	J.T. Baker	lab. grade	V, VI
anisole (methyl phenyl ether)	Merck	> 99%	IV, VI
Sulfur- and oxygen-containing compounds:			
para-mercaptophenol	Aldrich	> 90%	II, III
para-(methylmercapto)phenol	Aldrich	> 98%	II
ortho-mercaptoanisole	Aldrich	97%	IV
meta-mercaptoanisole	Aldrich	95%	IV
para-mercaptoanisole	Aldrich	95%	IV
para-(methylmercapto)anisole	Aldrich	99%	IV
Solvents:			
n-hexane	Rathburn	HPLC grade	I–III
	Baker	> 95%	IV
hexadecane	Fluka	> 98%	I, II, IV
meta-xylene	Merck	> 99%	I–VI
Tracer:			
decane	Fluka	> 99.5%	I–IV

[a] Alternative name of the compound in parenthesis.

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2.2 Reactors and procedures

As mentioned above, a batch reactor system was used to determine the extent to which the competition of the hetero atom removal reactions affects the efficiency of HDO and HDS [I-IV], and a flow reactor was used to study the stability of the catalyst during HDO [V, VI].

The batch reactor was a 50 cm^3 stainless steel autoclave equipped with a Robinson Mahoney-type catalyst basket. The reactions were carried out using a constant volume of the liquid phase, 16 cm^3 [I-IV]. The catalyst was packed to the reactor with two thirds of the reaction solvent. Hexadecane was chosen as solvent because of its low vapour pressure. For reactants insoluble in hexadecane, *meta*-xylene was used instead. The reactor was heated to the reaction temperature and the solutions of the substrates were added via a high pressure feed vessel. The reactions were carried out at temperatures between 150 and 280 °C and at a total pressure of 6.2–8.7 MPa. Higher reaction temperatures were avoided in order to minimise the formation of coke and high molecular weight contaminants on the catalyst. Four to six samples were withdrawn from the reactor liquid phase via a special sampling line of low volume (< 0.2 cm^3).

The flow reactor was a stainless steel tube reactor having an inside diameter of 10 mm and a length of 380 mm. The gas and liquid feed rates were adjusted to 2 dm^3(NTP)/h and 10 g/h, respectively, with mass flow controllers and were preheated to the reaction temperature in a vessel filled with silicon carbide. The catalyst (500 mg) was used in oxide form after calcination or sulfided in situ before use. The reactions were carried out at 200–300 °C and at a total pressure of 1.5 MPa. *meta*-Xylene was used as a solvent.

2.3 Thermal reaction tests

Thermal reactions of mercaptobenzene, (methylmercapto)benzene, *para*-mercaptophenol, *para*-(methylmercapto)phenol, mercaptoanisole isomers, *para*-(methylmercapto)anisole, reaction solvents and decane tracer were studied under argon

in 1 cm^3 boron silicate glass ampoules at 180–290 °C in order to separate the non-catalytic thermal reactions from the catalytic ones [II, IV]. The method has been described by Vuori *et al.* [35].

2.4 Analytical methods

Feed mixtures and reaction products were analysed with a Hewlett-Packard gas chromatograph 5890 A [I-IV] or a Hewlett-Packard gas chromatograph 6890 A [V, VI], both equipped with a flame ionisation detector (FID). The columns used for the separation of compounds were capillary columns DB-1 (length 60 m, film thickness 1.0 μm, column diameter 0.25 mm, J & W Scientific) [I-VI], SE-30 (length 30 m, film thickness 0.25 μm, column diameter 0.32 mm, Supelco) [I, II] and HP-1 (length 60 m, film thickness 1.0 μm, column diameter 0.25 mm, Hewlett Packard) [V, VI]. Impurities in some reagents and some reaction products were identified by gas chromatography and mass spectrometry (Hewlett-Packard gas chromatograph 5790, JEOL DX303/DA5000).

Sulfur and carbon contents of the catalysts were determined before and after the reactions with a Leco SC-444 analyser.

2.5 Phase equilibrium in the batch reactor

To compensate for the lack of quantitative gas phase analysis in the batch reactor studies, the gas phase composition in equilibrium with the analysed liquid phase was estimated with the PROCESS simulation program [36]. The amount of hydrogen dissolved in the reaction mixture was calculated simultaneously [II].

2.6 Conversions and kinetic parameters

Total conversions of HDO and HDS were defined as the conversions of oxygen and sulfur to H_2O and H_2S, respectively. For the individual reaction routes, conversions of the model compounds were calculated on the basis of the formation of compounds

containing either a benzene or an alicyclic ring. The selectivity for each ring-containing product was defined as its molar fraction of the sum of the ring-containing products.

The data obtained from the batch reactor were evaluated using a pseudo first-order rate equation (1) (in some cases a second-order rate equation) for potential simultaneous and/or consecutive reactions [I, III, IV]:

$$rate = k'*m_{cat}*C_A \tag{1}$$

In order to improve the comparability of the reaction data obtained in different reaction solvents, the initial concentration of hydrogen in the liquid phase was separated from the pseudo rate constant [II]. The calculations were carried out by the MODEST model estimation program [37].

3 RESULTS AND DISCUSSION

3.1 Activity of the catalyst during simultaneous HDO and HDS

Simultaneous HDO and HDS was studied to find out whether the HDO activity of a presulfided catalyst could be maintained in the presence of a sulfur-containing co-reactant, with effective removal of oxygen and sulfur at the same time. In addition to binary mixtures, simultaneous HDO and HDS was studied with disubstituted model compounds having an oxygen-containing substituent (hydroxyl or methoxy) and a sulfur-containing substituent (mercapto or methylmercapto) in the same benzene ring. Hydrotreating experiments were carried out in a batch reactor. The reaction pathways and the reaction parameters of HDO and HDS were compared with those of HDO and HDS of corresponding mono-substituted model compounds. Phenol and mercaptobenzene were chosen as reference molecules for HDO and HDS, respectively. In addition, the effect of a low molecular weight sulfiding agent, CS_2, on the rate parameters and on the reaction selectivities of the HDO paths of phenol and anisole was preliminarily tested.

3.1.1 HDO and HDS reference reactions in a batch reactor

Under the conditions studied, HDS of mercaptobenzene proceeded without changes in the ring structure, whereas HDO of phenol resulted in the formation of both aromatic and alicyclic reaction products, the aromatic product dominating, however [I]. In the path to alicyclics, formation of the corresponding hydrogenated alcohol, cyclohexanol, sometimes reported as an intermediate in HDO [13], was not detected. Diphenylsulfide was formed in a side reaction of mercaptobenzene, but no formation of the corresponding oxygen-containing compound, diphenylether, was detected with phenol. The HDS rate of mercaptobenzene was clearly higher than the HDO rate of phenol, and at 250 ºC, for example, the HDS rate was about 30-fold the HDO rate. On the basis of the observations, the simplified reaction networks of these compounds can be summarised as presented in Figures 2 and 3. In the following discussion, the reactions of phenol to benzene (Figure 2, path 1, marked with *) and alicyclics (Figure 2, path 2, marked with *) and of mercaptobenzene to benzene (Figure 3, path 1, marked with *) are used as reference reactions for HDS and HDO, respectively. Calculation of the equilibrium constants indicated that these reactions are virtually irreversible under the reaction conditions used [I].

Though it is well known that more complicated rate equations are needed for complete description of HDO and HDS reactions, pseudo first-order reaction models have commonly been used in screening the reactivities of model compounds [13,27]. In this work, the initial concentration of the substituents containing the hetero atom as well as the liquid volume of the reactor were kept constant within each series of experiments, and because hydrogen pressures were high the concentration of hydrogen in the liquid phase of the batch reactor remained almost constant during each run up to moderate conversions. This fixation of the reaction conditions makes the use of pseudo first-order rate equations feasible. The applicability of the parameters calculated for the reactions is, of course, limited to the reaction conditions employed. Thus, any comparisons with values reported in the literature for different experimental conditions are of doubtful value. Furimsky [13] adds a similar caution in his HDO review.
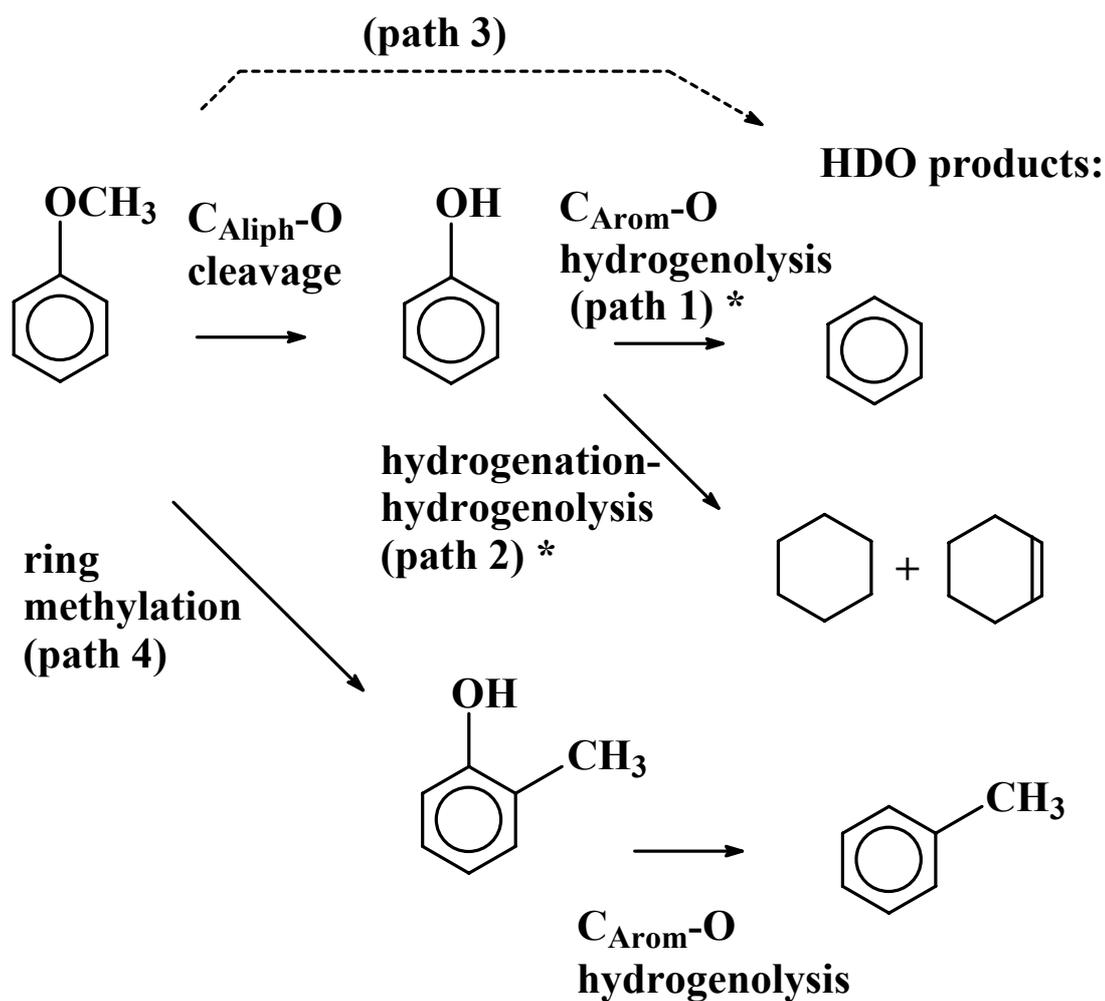
Figure 2. Simplified reaction networks of phenol and anisole. The HDO reference reactions are marked with *.

The apparent activation energies (E) determined for the HDO reference reactions were 112 kJ/mol for the reaction of phenol to benzene and 52 kJ/mol for the reaction to alicyclics. Thus, the apparent activation energy was clearly higher for the C_{Arom}–O hydrogenolysis than for the hydrogenation–hydrogenolysis route. The selectivities of the HDO routes as well as the apparent activation energies of the reactions were in fairly
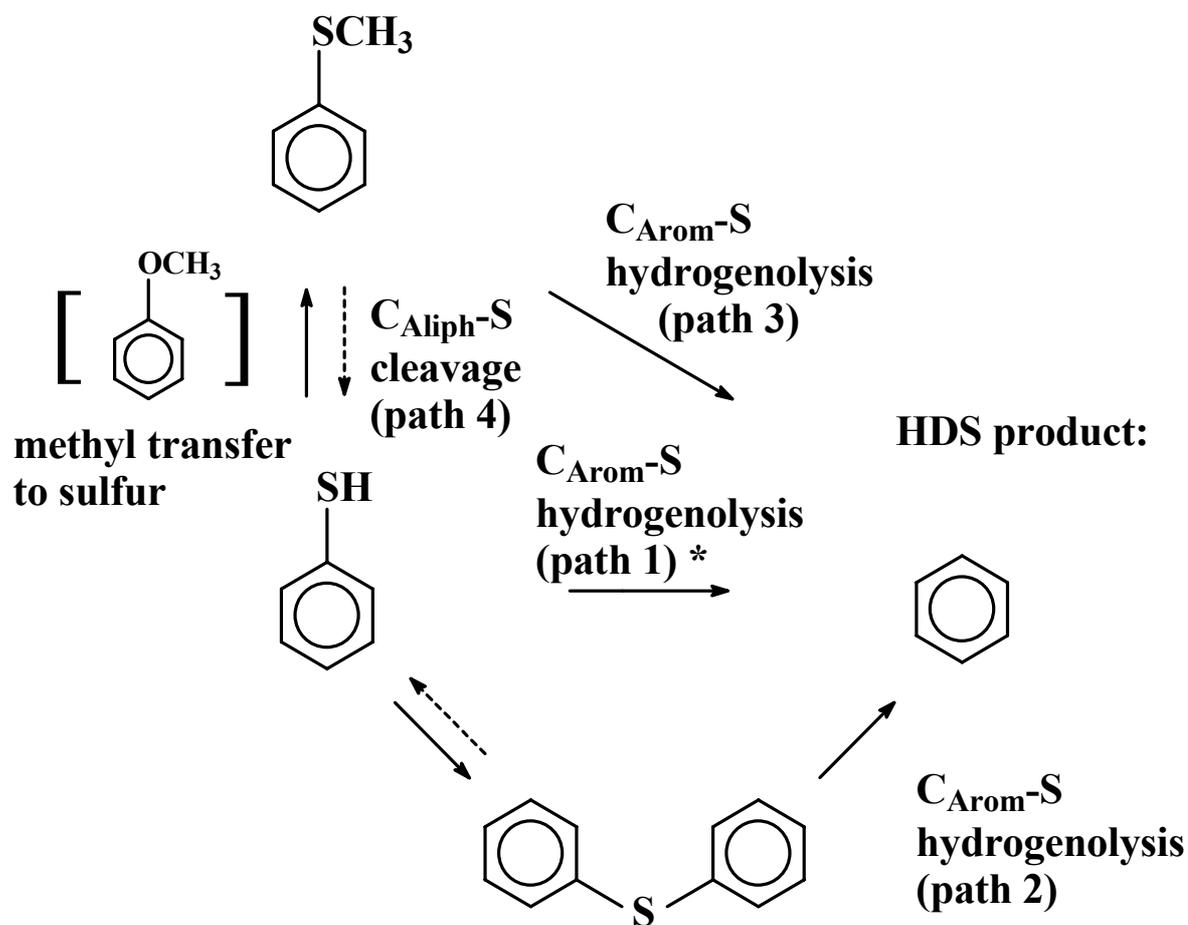
Figure 3. Simplified reaction networks of mercaptobenzene, diphenylsulfide, (methylmercapto)benzene and mercaptobenzene in the presence of anisole. The HDS reference reaction is marked with *.

good agreement with those determined for methylphenols and dimethylphenols on a sulfided CoMo/Al$_2$O$_3$ by Gevert *et al.* [38, 39].

The apparent activation energy for the C$_{Arom}$–S hydrogenolysis was lower than that for the C$_{Arom}$–O hydrogenolysis being 82 kJ/mol for the HDS reference reaction. Recent HDS studies reported in the literature have concentrated on thiophenic sulfur compounds because these are the least reactive organosulfur compounds in fossil fuels [27].

Therefore, reference values for the apparent activation energy of mercaptobenzene were not found.

For comparison, hydrotreating of mercaptobenzene was studied both in hexadecane and in *meta*-xylene. The HDS rate for mercaptobenzene was somewhat lower in *meta*-xylene than in hexadecane in spite of the better solubility of hydrogen in *meta*-xylene. The difference may be a consequence of the stronger adsorption of *meta*-xylene than of hexadecane on the catalyst. The apparent activation energy for the reaction in *meta*-xylene, 84 kJ/mol, was about equal to that in hexadecane, however. In a study of solvent effects in HDS of benzothiophene and dibenzothiophene on a CoMo/Al$_2$O$_3$ catalyst, Ishihara *et al.* [40] found that the apparent activation energy was almost independent of the solvent employed, but the heats of adsorptions of the sulfur compounds were affected by competitive adsorption of the solvents. In parameter fitting of our work, the numerical value calculated for the apparent activation energy was to some extent dependent on whether the initial concentration of hydrogen in the liquid phase of the reactor was taken into account or not: lower values of E were obtained with the rate models in which the hydrogen concentration was separated from the reaction rate constants [II]. In order to ensure the comparability of the parameters reported later in this study, the reaction data of the model compounds of paper II were recalculated using the reaction rate equation (1).

Below, the HDO rates for different mono- and disubstituted model molecules with oxygen-containing substituents are presented as relative reaction rates at 250 °C, where the value 100 is given for the initial rate of the direct hydrogenolysis of the C$_{Arom}$–O bond of phenol to benzene (see Table 3). A lower reference temperature was used for HDS reactions in view of the higher reactivity of the sulfur-containing groups, and the initial rate of the C$_{Arom}$–S hydrogenolysis of mercaptobenzene to benzene at 225 °C was given the value 100. The HDS rates of other sulfur-containing reaction systems are presented in relation to this reference value (see Table 4).

Table 3. Relative HDO rates of oxygen-containing model molecules at 250 °C.

Model molecule(s)	Relative reaction rate[a]		Ref.
	C_{Arom}–O hydrogenolysis	hydrogenation–hydrogenolysis route	
Monosubstituted oxygen compounds: phenol, solvent: *meta*-xylene	100	65	III
anisole, solvent: hexadecane	-[b]	-[b]	IV
Disubstituted model compounds: *para*-mercaptophenol, solvent: *meta*-xylene	15	7	III
Binary mixtures: phenol + mercaptobenzene, initial molar ratio 1:1	≈0	≈0	III
phenol + CS$_2$, initial molar ratio 10:1, solvent: *meta*-xylene	3	43	III
phenol + CS$_2$, initial molar ratio 2:1, solvent: *meta*-xylene	4	13	III
anisole + mercaptobenzene, initial molar ratio 1:1, solvent: hexadecane	≈0	≈0	IV

[a] Reference rate: initial rate of the direct hydrogenolysis of the C_{Arom}–O of phenol to benzene was assigned the value 100 (see Figure 2, path 1).

[b] Not determined. Total HDO of the magnitude predicted from the reaction rate of phenol under similar reaction conditions.

Table 4. Relative HDS rates of sulfur model molecules at 225 °C.

Model molecule(s)	C_{Arom}–S hydrogenolysis: relative reaction rate[a]	Ref.
Monosubstituted sulfur compounds:		
mercaptobenzene, solvent: hexadecane	100	IV
mercaptobenzene, solvent: *meta*-xylene	86	III
(methylmercapto)benzene, solvent: hexadecane	31	IV
diphenylsulfide, solvent: hexadecane	44	I
Disubstituted sulfur compounds:		
para-mercaptophenol, solvent: *meta*-xylene	872	III
para-(methylmercapto)phenol, solvent: *meta*-xylene	122[b]	II
ortho-mercaptoanisole[c] ,solvent: hexadecane	93	IV
meta-mercaptoanisole[c], solvent: hexadecane	47	IV
para-mercaptoanisole[c], solvent: hexadecane	180	IV
Binary mixtures:		
mercaptobenzene + phenol, initial molar ratio 5:1, solvent: *meta*-xylene	57	III
mercaptobenzene + phenol, initial molar ratio 2:1, solvent: *meta*-xylene	58	III
mercaptobenzene + phenol, initial molar ratio 1:1, solvent: *meta*-xylene	58	III
mercaptobenzene + anisole, initial molar ratio 1:1, solvent: hexadecane	69	IV

[a] Reference rate: initial rate of the C_{Arom}–S hydrogenolysis of mercaptobenzene to benzene was assigned the value 100 (see Figure 3, path 1).

[b] Data from [II] recalculated with equation (1) at 225 °C.

[c] Total HDS rate to anisole and phenol.

3.1.2 Hydrotreating of monosubstituted model molecules

Methylation of the hydroxyl and mercapto groups revealed another difference in the behaviour of the oxygen- and the sulfur-containing compounds of similar structure during hydrotreating (II, IV). Both for anisole and for (methylmercapto)benzene, the bond between the hetero atom and the aromatic carbon (C_{Arom}) is said to be stronger than the bond between the hetero atom and the aliphatic carbon (C_{Aliph}) [13,41]. In that case, the bond with the aliphatic carbon would more probably be broken, and phenol and mercaptobenzene, respectively, would be formed as intermediate products in total removal of the hetero atom. Earlier, Huuska [42] and Huuska and Rintala [43] ruled out the direct splitting of a methoxy group of anisole. In addition, Hurff and Klein [44] suggested that HDO of anisole proceeds via a phenol intermediate. Relevant to this, evaluation of the reaction data of paper IV supports the intermediate role of phenol: the reaction rate constants for the routes to HDO products directly from anisole (Figure 2, combined as path 3) were below the determination limit. Small amounts of ring-methylated reaction products were detected with the model compound containing methoxy group but not with (methylmercapto)benzene.

In the case of (methylmercapto)benzene, the dominating HDS route was direct hydrogenolysis of the C_{Arom}–S bond (Figure 3, path 3) rather than C_{Aliph}–S cleavage (Figure 3, path 4). Only very small amounts of mercaptobenzene were detected, although HDS of alkylarylsulfides on sulfide catalysts have been described in the literature as proceeding via this intermediate, in analogy with alkylarylethers [45]. The dominance of direct hydrogenolysis of the C_{Arom}–S bond was supported by an evaluation of the reaction data: the rate constant for the C_{Aliph}–S cleavage was below the determination limit [II]. As a whole, the rate of C_{Arom}–S hydrogenolysis was noticeably lower for the sterically more hindered sulfide structures, (methylmercapto)benzene and diphenylsulfide, than for mercaptobenzene (see Table 4).

For anisole, the apparent activation energy for the reaction to phenol was 99 kJ/mol (see Table 5). A higher value, 124 kJ/mol, is reported by Hurff and Klein [44]. In their study,

however, CS$_2$ was present in the reaction mixture. Further comparison with values reported in the literature is not really possible because in most of the studies the values were determined only for the disappearance of the oxygen-containing starting material and not for the formation of the reaction products via different routes [13]. In analogy with the reactions of anisole, oxygen-containing intermediates are probably formed when more complex oxygen model compounds are hydrotreated, and the total oxygen removal rate is not congruent with the rate of disappearance of the oxygen- containing starting molecule. The apparent activation energy was higher for (methylmercapto)benzene than for mercaptobenzene (see Table 6). Reference data for alkyl- and aryphenylsulfides were not found.

Table 5. Apparent activation energies, E, for reactions of oxygen-containing model molecules.

Model molecule(s)	Reaction	E, kJ/mol	Ref.
phenol	C$_{Arom}$–O hydrogenolysis	112	II
	hydrogenation-hydrogenolysis	52	II
anisole	C$_{Aliph}$–O cleavage	99	IV
	C$_{Arom}$–O hydrogenolysis	-[a]	IV
	hydrogenation–hydrogenolysis	-[a]	IV
anisole + CS$_2$ • initial molar ratio 10:0.3 • initial molar ratio 10:0.7	C$_{Aliph}$–O cleavage C$_{Aliph}$–O cleavage	111 112	IV IV
anisole + mercaptobenzene • initial molar ratio 1:1	C$_{Aliph}$–O cleavage	64	IV

[a] HDO rate too low for determination of the apparent activation energies.

Table 6. Apparent activation energies, E, for HDS reactions of model molecules.

Model molecule(s)	Reaction	E, kJ/mol	Ref.
mercaptobenzene • solvent: hexadecane • solvent: *meta*-xylene	C_{Arom}–S hydrogenolysis C_{Arom}–S hydrogenolysis	82 84	IV III
(methylmercapto)benzene	C_{Arom}–S hydrogenolysis	104	IV
diphenylsulfide	C_{Arom}–S hydrogenolysis	97	I
para-mercaptophenol	C_{Arom}–S hydrogenolysis	100	III
para-(methylmercapto)phenol	C_{Arom}–S hydrogenolysis	106[a]	II[a]
para-mercaptoanisole	formation of anisole formation of phenol	93 112	IV IV
phenol + mercaptobenzene • initial molar ratio 1:1	C_{Arom}–S hydrogenolysis	126	III
anisole + mercaptobenzene • initial molar ratio 1:1	C_{Arom}–S hydrogenolysis	81	IV

[a] Data from [II] recalculated with equation (1) at 225 °C.

3.1.3 Simultaneous HDO and HDS

The effect of possible competition of the HDO and HDS reactions on their rates and selectivities was studied with model compounds having a sulfur-containing and an oxygen-containing substituent in the same molecule [II-IV], and with binary mixtures of mono-substituted benzene model compounds [III, IV]. Although the disubstituted benzenes used in this study are at best theoretical models of real mixtures of crude oil and biocrudes, investigation of their reactions can give information on reaction pathways and on the species adsorbed on the active sites during simultaneous HDO and HDS.

The disubstituted model compounds had either a hydroxyl or a methoxy group as the oxygen-containing substituent and either a mercapto or a methylmercapto group as the sulfur-containing substituent. In studies with binary mixtures, either phenol or anisole was used as the oxygen-containing and mercaptobenzene as the sulfur-containing model compound.

The experiments with the disubstituted benzenes and the binary mixtures of mono-substituted benzenes both revealed the dominating role of the sulfur-containing substituent: oxygen removal did not start until the HDS conversion was almost complete. In the early stages of HDO, the combined hydrogenation–hydrogenolysis route was favoured. Later, formation of the aromatic HDO product, benzene, slowly increased [III] when the active sites for hydrogenolysis became available for adsorption via the oxygen atoms.

Methyl transfer to sulfur was noticeable in hydrotreating of the compounds having a methoxy group present in the same molecule with the sulfur substituent and in hydrotreating of the binary mixtures containing anisole and mercaptobenzene. Because the reactivity of the methylmercapto group is lower than that of the original mercapto group, the rate of HDS decreased as a consequence. In contrast to studies of Toropainen *et al.* [46], products containing sulfur but no oxygen were not detected, and no mercaptophenol was formed in the reactions of mercaptoanisole isomers and (methylmercapto)phenol. The broader product distribution found by Toropainen *et al.* is probably explained by the presence of a wider range of active sites on their catalyst due to presulfidation at lower temperature as well as by the type of the reaction system. On the basis of our observations, simplified reaction networks can be presented for the disubstituted model molecules (Figure 4).

Electronic effects determined the order of the HDS reactivity of the disubstituted model compounds. An electron releasing substituent in *para*-position to the sulfur-containing group increased the HDS rate noticeably [II-IV]. This was probably due to an increase in the electronegativity of the sulfur atom caused by the presence of the substituent. A
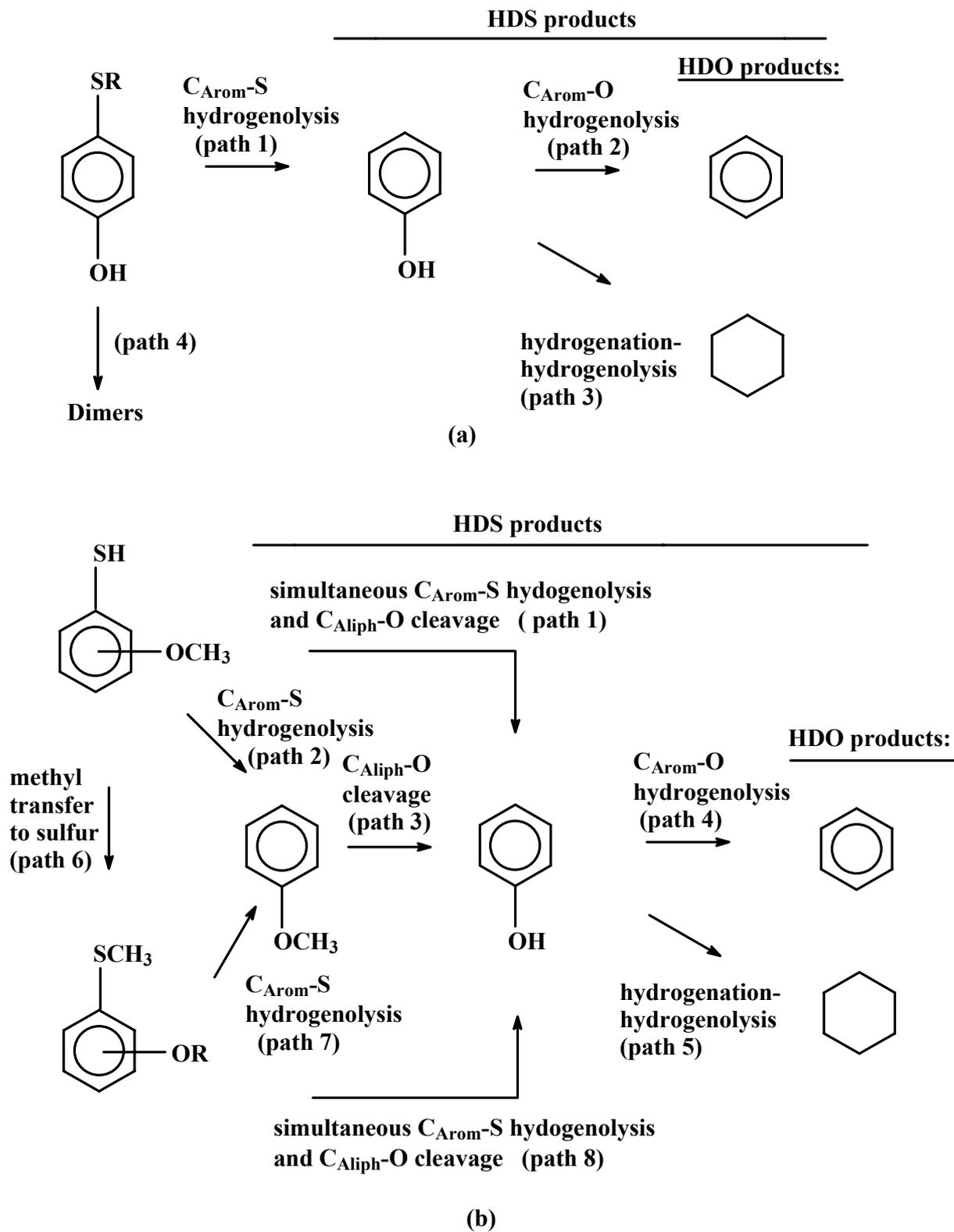
HDS products

HDO products:

SR
C$_{Arom}$-S
hydrogenolysis
(path 1)

C$_{Arom}$-O
hydrogenolysis
(path 2)

OH

(path 4)

Dimers

hydrogenation-
hydrogenolysis
(path 3)

(a)

HDS products

SH

simultaneous C$_{Arom}$-S hydogenolysis
and C$_{Aliph}$-O cleavage   (path 1)

OCH$_3$

C$_{Arom}$-S
hydrogenolysis
(path 2)

C$_{Aliph}$-O
cleavage
(path 3)

HDO products:

C$_{Arom}$-O
hydrogenolysis
(path 4)

methyl
transfer
to sulfur
(path 6)

SCH$_3$

OCH$_3$

OH

OR

C$_{Arom}$-S
hydrogenolysis
(path 7)

hydrogenation-
hydrogenolysis
(path 5)

simultaneous C$_{Arom}$-S hydogenolysis
and C$_{Aliph}$-O cleavage   (path 8)

(b)

Figure 4. Simplified reaction networks of (a) *para*-mercaptophenol and *para*-
(methylmercapto)phenol   and   (b)   mercaptoanisole   isomers.

similar phenomenon has been reported by Konuma *et al.* [47] as a difference in the conversions of mercaptoanisole isomers and mercaptobenzene on a MoS$_2$ catalyst. Evaluation of our reaction data showed the HDS rate of *para*-mercaptophenol to be about an order of magnitude higher than that of mercaptobenzene at 225 °C and the rate of *para*-(methylmercapto)phenol was about fourfold that of (methylmercapto)benzene [II] (see Table 4). In the presence of a *para*-methoxy group, the HDS rate of a mercapto group was doubled. The positive effect of a *para*-methoxy group on the HDS rate is partially compensated by methyl transfer to sulfur, producing a methylmercapto substituent more resistant to hydrotreating [IV]. A methoxy group in *ortho* position to the mercapto group did not affect the HDS rate in *ortho*-mercaptoanisole, but in the presence of a *meta*-methoxy group, the HDS rate of the mercapto group was about halved.

The structure of the isomer controlled the product selectivity of HDS of the mercapto-anisoles: phenol was the main product of *ortho*-mercaptoanisole, whereas anisole was the main product of both the *meta*- and the *para*-isomer [IV]. In addition, methyl transfer to sulfur was strongest with the *ortho*-compound. In *ortho*-mercaptoanisole, the vicinity of the substituents makes possible the simultaneous reaction of both substituents: the contact between the methoxy group and the catalyst surface is easier in the surface complex formed either by adsorption via the sulfur atom or via flat coplanar chemisorption of the molecule.

The apparent activation energies, E, for HDS of mercapto and methylmercapto groups were higher for compounds having a hydroxyl group in *para*-position to the sulfur-containing group than for the corresponding mercaptobenzene and (methylmercapto)benzene compounds (see Table 6). Moreover, the E values followed the order of electronegativity of the sulfur atom: a hydroxyl group in *para*-position to the sulfur atom increased the electronegativity of the sulfur atom, and methylation of the mercapto group increased it further. This finding together with the reactivity data is in accordance with the studies of Konuma *et al.* [48] who calculated the electronic states of

mercaptoanisole isomers using a semi-empirical molecular orbital method. They observed that the HDS reactivity of the isomers followed the order of frontier π-electron densities of both the sulfur atoms and the *ipso*-carbons. For the mercaptoanisole isomers, the apparent activation energies were calculated for the formation of anisole and for the formation of phenol from the *para*-isomer and the values of E can only be considered as trendsetting because of the complex reaction network of the compound [IV]. The differences in E values indicate a difference in the HDS reaction mechanism of the mercapto group in the disubstituted benzenes and in mercaptobenzene: apparently the increased electron density of the sulfur atom in the presence of a *para*-hydroxyl or a *para*-methoxy group facilitates the adsorption of the compound to the electrophilic hydrogenolysis site of the catalyst and, at the same time, the rate of HDS is increased. [II–IV].

In binary mixtures, the HDS rate of mercaptobenzene at 225 °C decreased by 20–30% in the presence of either phenol or anisole [III, IV]. No reaction of phenol was detected, however, until practically all mercaptobenzene had disappeared. The apparent activation energy of the HDS reaction of mercaptobenzene increased, indicating that either the mechanism of HDS changed due to the presence of phenol or, more probably, that competitive adsorption of phenol as an inhibitor and the temperature dependency of this adsorption should be taken into account in the HDS rate equation. The strong adsorption of the oxygen compounds is known: the self-inhibiting effect of oxygen-containing compounds on HDO has been noted in several kinetic studies [13]. In addition, the strong adsorption of the oxygen-containing compounds has been reported in simultaneous HDS and HDO; in the case of benzothiophene and benzofuran, for example, the adsorption constant calculated for benzofuran was about sixfold that for dibenzothiophene [49].

As mentioned above, methyl transfer to sulfur was notable, and (methylmercapto)benzene was formed from mercaptobenzene in the presence of anisole (see Figure 3). As a consequence, the HDS rate decreased noticeably, and the formation of ring-methylated products of anisole was totally suppressed. This tendency of the sulfur

atom to capture a methyl group resulted, on the other hand, in a noticeable increase in the C_{Aliph}–O cleavage rate of anisole. In evaluation of the reaction data, the apparent activation energy of the demethylation reaction of anisole was found to be much lower than the value calculated for the reaction in the absence of the sulfur-containing co-reactant indicating a change in the mechanism of the reaction in the presence of mercaptobenzene (see Table 5). This change is clearly seen in the contour lines of the reaction parameters presented in Figure 5: the lines for anisole in the absence (a) and in the presence (b) of mercaptobenzene are clearly separated. The apparent activation energy for the HDS reaction of the mercapto group was not affected by the presence of anisole.

3.1.4 Effect of CS$_2$ on HDO in a batch reactor

The effect of CS$_2$ on HDO of phenol and anisole was studied to determine the effect of a low molecular weight sulfiding agent on the activity of the presulfided catalyst and on the selectivity of the HDO reaction paths. The HDO rate of phenol decreased noticeably in the presence of CS$_2$, and the selectivities of the HDO reaction paths were changed as the hydrogenation–hydrogenolysis route was less sensitive to the sulfur compound than was the C_{Arom}–O hydrogenolysis [III, IV]. At higher concentrations of the sulfiding agent, the hydrogenation route became inhibited as well (see Table 3). The inhibition of HDO is probably stronger at early stages of the reaction due to the presence of methyl mercaptan formed as an intermediate in the reaction path from CS$_2$ to H$_2$S. In the case of anisole, CS$_2$ seems to act as a methyl capturer and to promote the demethylation reaction of anisole in some degree. Unlike some earlier studies [33], no increase was detected in the hydrogenation activity of the catalyst that would indicate interconversion of the active sites due to the presence of H$_2$S.

The apparent activation energy for the C_{Aliph}–O cleavage of anisole increased in the presence of CS$_2$ and approached the value proposed by Hurff and Klein [44]. However,
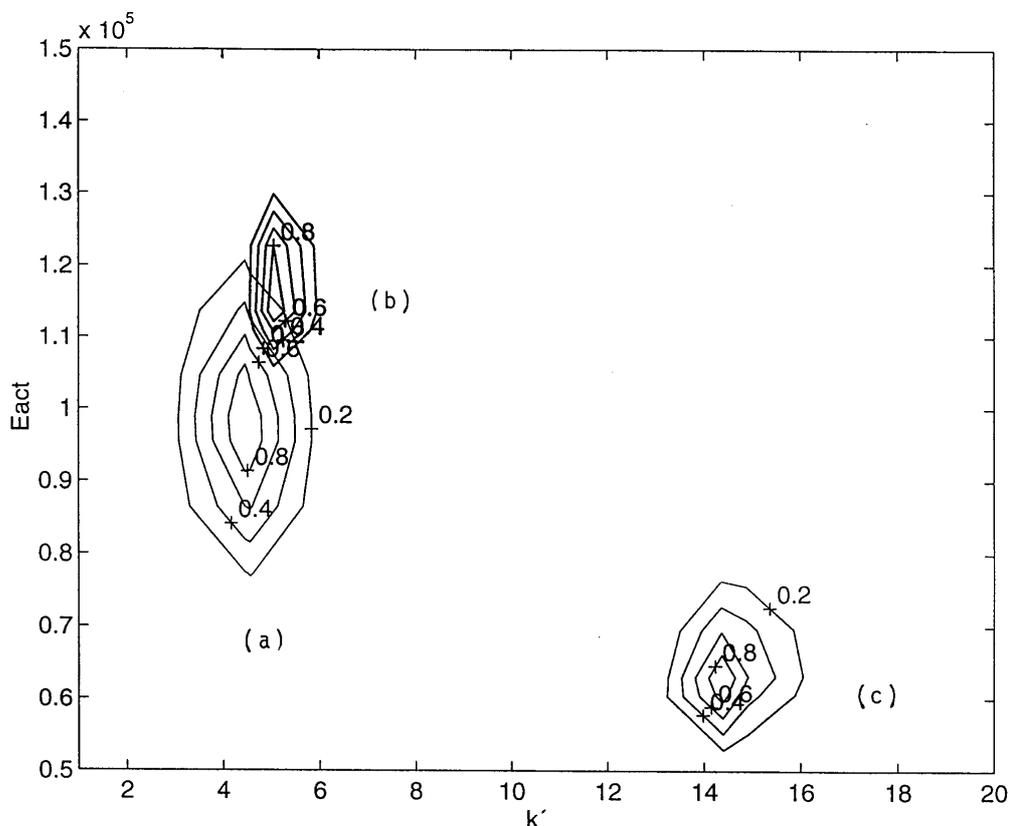
Figure 5. Contour lines for the parameters of (a) anisole, (b) anisole in the presence of CS$_2$ and (c) anisole in the presence of mercaptobenzene (E = () kJ/mol, k´= () g$_{cat}^{-1}$h^{-1}) [IV].

the contour lines of the reaction parameters for the C$_{Aliph}$–O cleavage reaction of anisole (a) and the same reaction in the presence of CS$_2$ (b) partially overlapped (see Figure 5). Conclusions regarding changes in the reaction mechanism cannot be reliably drawn, therefore, in contrast to the case of anisole and mercaptobenzene. It is nevertheless possible that the positive effect of CS$_2$ on the demethylation is partially caused by resulfidation of the catalyst and partially by a bimolecular reaction between the methoxy group and CS$_2$ adsorbed on the catalyst proceeding in parallel with the original demethylation reaction.

3.1.5 Summary of simultaneous HDO and HDS

In summary, simultaneous HDO and HDS of substituted benzenes at relatively low hydrotreating temperatures and at about 7 MPa led to total suppression of the HDO reactions of hydroxyl and methoxy groups as long as sulfur-containing reactants were present in the reaction system. HDS reactions were either retarded or enhanced. HDS was enhanced if the oxygen atom was located in a substituent attached in *para*-position in the same molecule as the sulfur substituent. Otherwise the HDS rate decreased due to competitive adsorption of the oxygen-containing compound and, in the presence of methoxy substituents also due to methyl transfer to sulfur, leading to a less reactive methylmercapto compound. At 225 °C, the rate of HDS of the reaction systems decreased in the order presented in Figure 6.
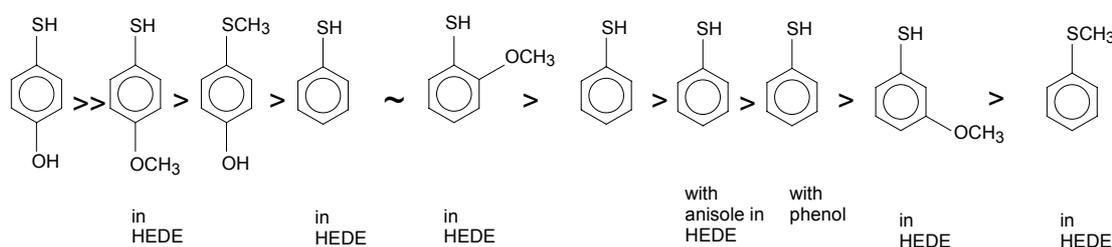

Figure 6. HDS rate order of substituted benzenes at 225 °C. HEDE, hexadecane used as solvent; otherwise *meta*-xylene.

3.2 Stability of the catalyst during HDO

Although a batch reactor is very useful for reactivity studies, it cannot provide information on the stability of the catalyst. A flow system is required for that purpose. Accordingly, HDO of phenol and anisole was further studied in a flow reactor in the absence and presence of sulfiding agents a) to see whether such an agent is needed to

keep up the activity of the presulfided catalyst during hydrotreating of oxygen-containing feeds and b) to see whether the oxide form of the catalyst can be activated by sulfidation during HDO [VI]. In addition, the effect of alternating periods of HDO and HDS on the stability of the presulfided catalyst was tested to obtain information on the sensitivity of the catalyst to changes in the feed composition [V]. HDS of benzothiophene was used as a standard test for the hydrotreating activity of the catalyst. Very few earlier papers have dealt in a comprehensive way with the stability of the presulfided catalysts during HDO [50-53].

3.2.1 HDO and HDS in a flow reactor

No reaction products other than those found in the batch experiments were detected in flow experiments made with phenol on the presulfided catalyst in the absence of sulfiding agents. As in the batch reactor studies, the direct C_{Arom}–O hydrogenolysis of phenol to benzene was strongly favoured over the hydrogenation–hydrogenolysis route to alicyclics (see Figure 7). The HDO activity of the oxide form of the catalyst was negligible.

The HDO activity of the presulfided catalyst decreased rapidly with time on stream [V, VI]. The ring balance of phenol was >97% at 250 °C but decreased to about 92% at 300 °C, suggesting the formation of high molecular weight products or coke. The selectivities of the HDO paths were not affected by time on stream at 250 °C, however. This indicates that either the two reactions proceed on the same active site or two different active sites are involved, which deactivate at the same rate.

In general, when oxygen-containing feeds are hydrotreated on a presulfided CoMo/Al$_2$O$_3$ catalyst in the absence of sulfur or nitrogen compounds, the catalyst is exposed to at least three factors that may lead to deactivation. These are (1) formation of water in HDO reactions, (2) formation of coke and (3) formation high molecular weight deposits from the oxygen-containing molecules. In addition, the sulfide structure of the catalyst may be altered during HDO due to desulfurization. In their review dealing with the deactivation
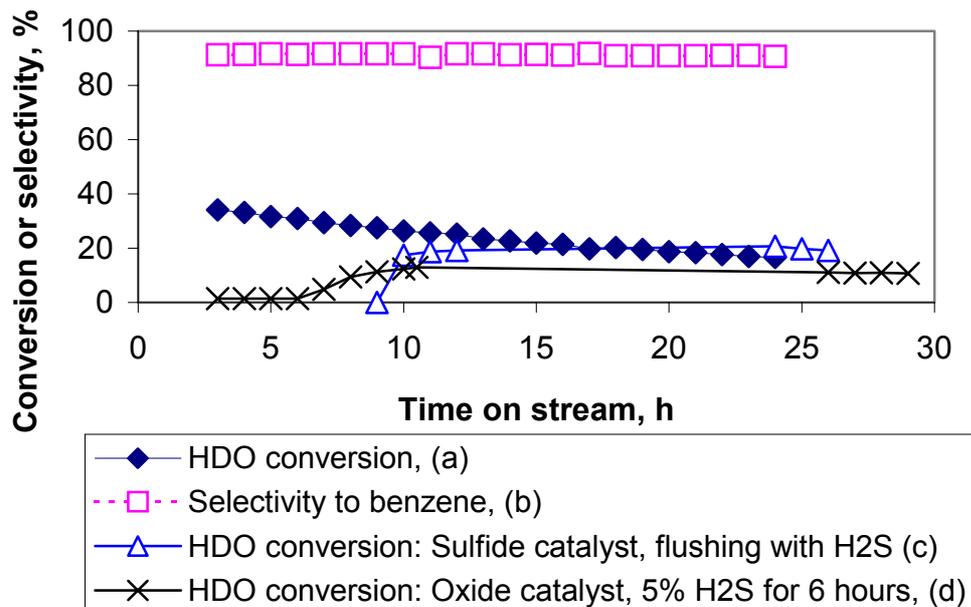
Figure 7. Stability of the CoMo/Al$_2$O$_3$ catalyst in HDO at 250 °C: (a) HDO conversion of phenol and (b) selectivity to benzene on the presulfided catalyst, (c) HDO conversion of phenol on the presulfided catalyst after 8 hours of HDO and subsequent flushing of the catalyst with 5% H$_2$S/H$_2$ for 1 hour, and (d) HDO conversion of phenol on the oxide catalyst in the presence of 5% H$_2$S/H$_2$ for 6 hours and after removal of H$_2$S from the feed [VI].

of hydrotreating catalysts, Furimsky and Massoth [28] observe that the poisoning effect of water may be quite significant when the water concentration is high, as in the hydroprocessing of biomass derived feeds. Some papers, they continue, report that the effect of water can be diminished by adding H$_2$S to the HDO feed. However, they also note some contradictory results on the effect of water. Laurent and Delmon [53] report that exposure of a presulfided NiMo/γ-Al$_2$O$_3$ catalyst to water in a batch reactor noticeably decreased the activity of the catalyst in subsequent HDO of 4-methylphenol, but the selectivity of the two HDO routes was not affected. In our study, the deactivation of the catalyst without change in the selectivity of the HDO paths may have been due to the formation of water. In addition, the degree of sulfidation of the catalyst decreased

during HDO of phenol, and in 24 hours of time on stream the sulfur content of the catalyst decreased by about 12%.

The presulfided catalyst also deactivated in the hydrotreating of anisole [VI]. The product distribution of anisole was more complex in the flow reactor than in the batch system (see Figure 2), and among others, the formation of *ortho*-methyl anisole, 2,6-xylenol and toluene was detected. Demethylation and methyl transfer to the benzene ring also proceeded effectively on the oxide form of the catalyst and on the γ-alumina support, but no HDO products were formed. This indicates that while presulfidation of the catalyst is needed for HDO, demethylation proceeds even on the acidic sites of the catalyst support. In the same way as with phenol, the distribution of the HDO products—benzene, alicyclics and toluene—remained virtually constant with time on stream.

In HDS of dibenzothiophene, both the activity and the selectivity of the presulfided catalyst stayed nearly constant, and ethylbenzene and dihydrobenzothiophene were formed as reaction products [V]. The activity of the oxide form of the catalyst increased slowly during HDS of benzothiophene due to sulfidation of the catalyst.

3.2.2 Effect of low molecular weight sulfiding agents on HDO

The oxide form of the catalyst did not show any HDO activity in hydrotreating of phenol in the presence of 5% of H_2S in the H_2 feed, but the activity of the catalyst was slowly established after removal of the sulfiding agent from the feed (see Figure 7, graph (d)) [VI]. The sulfur content of the oxide catalyst increased in 12 hours up to as much as 95% of the calculated sulfur content of a properly sulfided catalyst. The activity of the catalyst was lower than that of the presulfided catalyst, however, indicating that formation of the active sulfide structure is not effective in the presence of oxygen-containing compounds. On the other hand, the reaction temperature of HDO may have been too low for the formation of the active sulfide structure.

Deoxygenation of phenol on the presulfided catalyst was noticeably suppressed in the presence of sulfiding agents over the whole concentration range tested [VI]. In addition, the initial selectivity of HDO was strongly affected (see Figure 8). Little difference was seen in the effects of CS_2 and H_2S. In accordance with the batch reactor studies [III, IV] and the findings of Gevert *et al.* with methyl phenols [38,39], the sulfiding agent had more effect on the formation of the aromatic reaction product than on the route to alicyclics. The latter route remained practically unaffected up to the highest H_2S concentration (5%) in the H_2 feed. Such selective inhibition of the C_{Arom}–O hydrogenolysis route of HDO confirms the presence of at least two kinds of active sites on the catalyst. No improvement of the stability of the presulfided catalyst in the presence of sulfiding agents was detected, and the activity of the catalyst decreased with time on stream without detectable changes in the selectivities of the HDO routes [VI]. Thus, it seems that continuous addition of sulfiding agents to the HDO feed does not offer a way to maintain the activity of the presulfided catalyst during HDO, but in some degree it might be used to control the reaction selectivity of HDO through the selective inhibition of the route to aromatics.

A slight positive effect on the activity of the catalyst was achieved when the presulfided catalyst was flushed with 5% of H_2S in H_2 for one hour after an HDO period of phenol of eight hours (see Figure 7, graph (c)).

In hydrotreating of anisole on the presulfided catalyst in the presence of H_2S, the total conversion of anisole increased in the same way as in the batch reactor studies, but HDO was suppressed. No improvement in the stability of the catalyst was detected [VI]. As mentioned above, demethylation and ring-methylation reactions of anisole were also notable on the oxide form of the catalyst and on the γ-Al_2O_3 support. On the oxide catalyst, the demethylation conversion of anisole increased in the presence of H_2S. This suggests that the HDO and demethylation reactions proceed, at least in part, on different active sites of the CoMo/γ-Al_2O_3 catalyst: acidic sites of γ-Al_2O_3 are probably involved in demethylation reactions, and the positive effect of H_2S is probably due to the acidic sulfhydryl groups formed on the catalyst in the presence of H_2S [13,29].
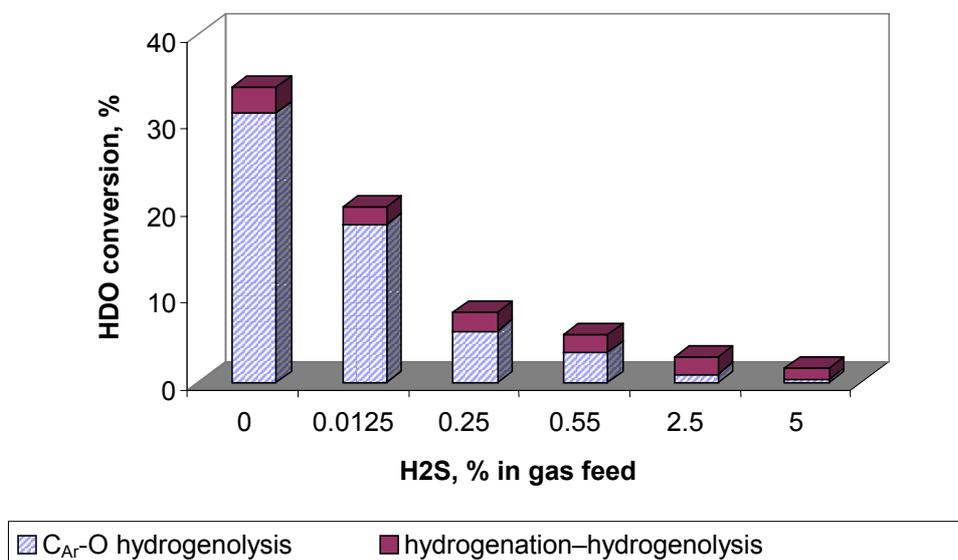
Figure 8. Effect of H$_2$S on the HDO routes of phenol [VI].

3.2.3 Alternating periods of HDO and HDS

The stability of the presulfided CoMo/γ-Al$_2$O$_3$ catalyst against changes in the feed composition was studied to see whether it would be possible to maintain the HDO activity of the catalyst through the use of alternating periods of HDO and HDS. Periods of four to eight hours of HDO of phenol and HDS of benzothiophene were tested [V].

A preceding HDS period had a positive effect on the stability of the presulfided catalyst in HDO. Furthermore, the positive effect was more pronounced when the reaction test was started with a HDS period: practically no deactivation of the catalyst was detected during any HDO period of eight hours and the selectivities remained constant. However, the total HDO conversion of phenol decreased by about 4 percentage units after each HDS period (see Figure 9 (a)). Moreover, both the total conversion and the HDS conversion of benzothiophene decreased after each HDO period. The HDS activity of the catalyst was slowly recovered on sulfur-containing feed due to the slow resulfidation

and/or restructuring of the catalyst. From the slope of the conversion curves in Figure 9 (b) it could be predicted that complete recovery of the catalyst activity would occur after an HDS period of about 20 hours.

In HDO of phenol in the absence of H_2S (see sect. 3.2.1), the catalyst was deactivated without any observable changes in the selectivities of the HDO routes, possibly due to one or several of the deactivating factors mentioned above. On the basis of our results it would seem possible to minimise the deactivation by carrying out a stabilising HDS period before initiating HDO. The activity might also be recovered during further HDS periods. The type of decrease in the activity of the catalyst detected between the HDO periods may be irreversible and caused by the competing period of HDO and HDS as the cycles change. That is, owing to the higher reactivity of the sulfur compound, hydrogen is consumed in HDS; there is not enough active hydrogen available for HDO, and the adsorbed oxygen compounds polymerize, decreasing the activity of the catalyst. Possibly this kind of deactivation could be reduced through the use of longer periods of HDS between the HDO cycles. Further studies are needed to determine the optimum length of the HDO and HDS periods.

4 CONCLUSIONS

Oxygen-containing compounds are present in abundance in biomass, and hydrodeoxygenation (HDO) is essential to improve the storage stability and properties of biomass-based liquids. HDO can be carried out by using the process developed for the hydrodesulfurization (HDS) of conventional oil fractions relying on presulfided $CoMo/Al_2O_3$ catalysts. The stability of the presulfided catalyst is critical in HDO because biocrudes typically do not contain the sulfur compounds needed to maintain the required level of sulfidation of the catalyst. The role of sulfur in HDO was studied in this work. Sulfur was introduced either as an organic sulfur-containing co-reactant or it
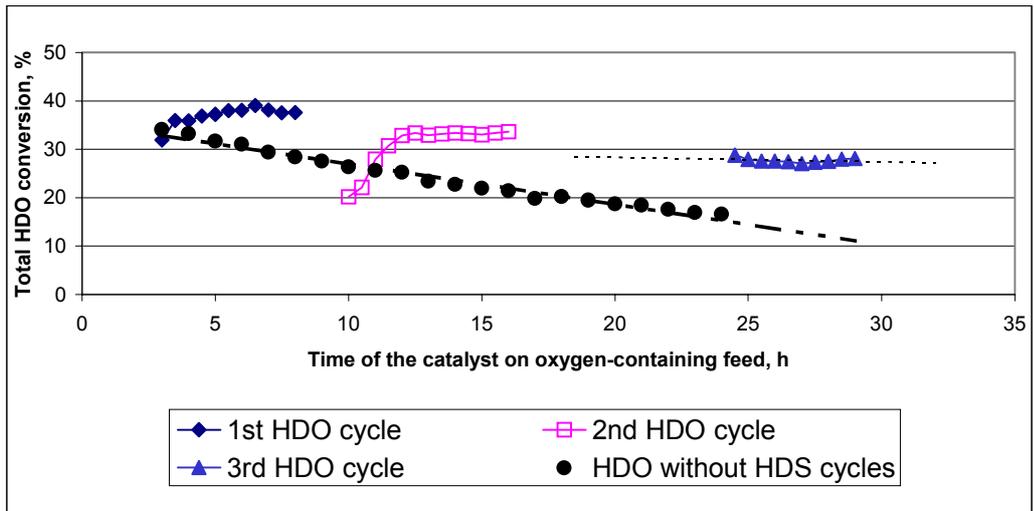
(a)
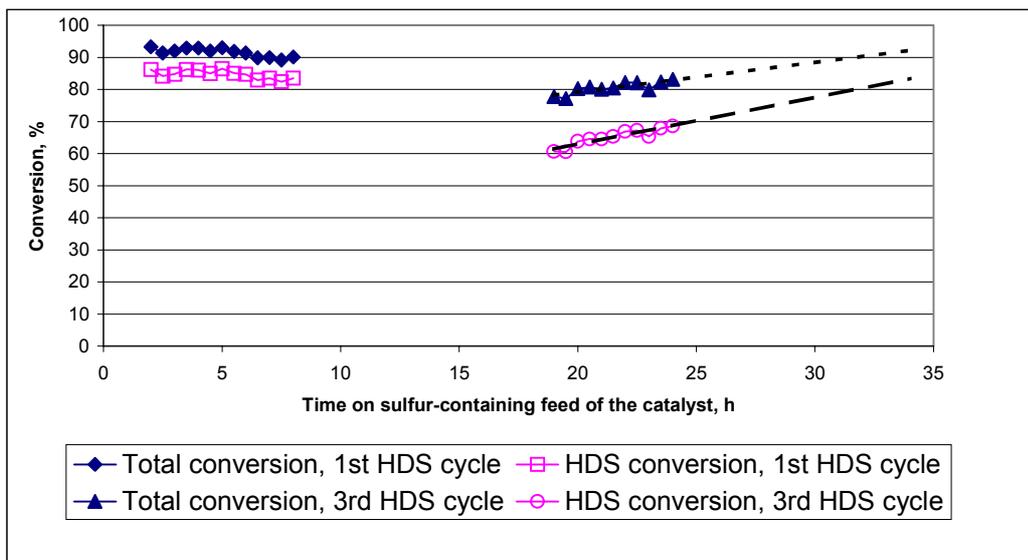
(b)

Figure 9. Alternating HDO and HDS: (a) effect of HDS cycles on HDO and (b) effect of HDO cycles on HDS [V].

was introduced as a sulfur-containing substituent in the oxygen-containing reactant, simulating feed mixtures composed of biocrudes and conventional crude oils from petroleum resources, or as a low molecular weight sulfiding agent, H_2S or CS_2. In addition, the stability of the presulfided catalyst against changes in feed composition was studied with use of alternating periods of HDO and HDS.

In simultaneous HDO and HDS, the HDO reactions of hydroxyl and methoxy substituents in the benzene ring were strongly suppressed, while the HDS reactions of mercapto and methylmercapto groups were either retarded or enhanced. Enhancement of HDS was only detected when the sulfur- and the oxygen-containing groups were present in an electronically favourable position in the same benzene ring. Otherwise, the HDS rate decreased due to strong competitive adsorption of the oxygen-containing compound on the active sites of the catalyst, and due to the formation of less reactive sulfur compounds via methyl transfer from the methoxy groups. Formation of these types of methyl transfer products in mixed feeds of biocrudes can be considered highly probable. Simultaneous HDO and HDS seems, therefore, not to be a solution to the problem of maintaining the active sulfided state of the catalyst during HDO.

Addition of low molecular weight sulfiding agents in the HDO reaction selectively affected the reaction paths of HDO. The presence of at least two kinds of active sites on the catalyst, one for hydrogenolysis and the other for hydrogenation reactions, was thereby confirmed. Up to moderate concentrations of the sulfiding agent, formation of the hydrogenated deoxygenation products remained constant, but the yield of the aromatic HDO product decreased dramatically. The catalyst deactivated with time on stream just as in the absence of sulfiding agent. The selective inhibition of one of the reaction paths could be used to adjust the product distribution but only at the cost of the total HDO conversion. Flushing the catalyst with H_2S in the absence of HDO feed had a slightly positive effect on the activity of the presulfided catalyst.

The most promising way to carry out HDO on a presulfided catalyst proved to be to process oxygen-containing and sulfur-containing feeds alternately. Deleterious

competition of HDO and HDS was almost completely avoided, additional sulfiding agents were not needed and the stability of the presulfided catalyst during the HDO periods was improved. The lengths of the HDS and the HDO periods still require optimization.

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