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# Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

# Competitive reactions and mechanisms in the simultaneous HDO of phenol and methyl heptanoate over sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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# A R T I C L E I N F O

Article history: Received 18 May 2010 Received in revised form 2 September 2010 Accepted 16 September 2010 Available online 14 October 2010

Keywords: Hydrodeoxygenation (HDO) Methyl heptanoate Phenol Sulphided NiMo Competitive reactions

# ABSTRACT

Hydrodeoxygenation (HDO) of phenol and methyl heptanoate separately and as mixtures was carried out over a sulphided NiMo catalyst to compare the HDO of aromatic and aliphatic reactants. Some experiments were also carried out in the presence of a sulphur additive. The conversion of phenol was suppressed in the presence of methyl heptanoate, whereas the conversion of methyl heptanoate was practically unaffected by phenol. In addition, distributions of the hydrocarbon products were different for reactants in the mixture and the reactants tested separately. Sulphur additive changed the product distribution of the separate components more than that of the mixture. The findings indicate that reduction (including hydrogenation) reactions occur on coordinatively unsaturated sites (CUS) independently of the aromatic or aliphatic character of the component. Sulphur, too, adsorbs on CUS and competes with other reactants that have an affinity to CUS. Decarbonylation and acid-catalysed reactions are, instead, proposed to occur on sulphur-saturated sites.

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# 1. Introduction

Concern over the impact of fossil fuels on the environment is driving a quest for suitable, environmentally friendly alternatives for fuels. Biomass-based liquids are considered as one option, either as fuel components or as fuels in their own right. Wood-based biooils and vegetable-based fatty acid methyl esters (FAME) can be mixed with fossil fuels only in small amounts, however, because of their high oxygen content. In addition, their energy content is lower than that of fossil fuels. Hydrodeoxygenation (HDO) [1], in which oxygen is totally or partly removed under H<sub>2</sub> pressure, is a proven method for upgrading these mixtures to the required quality.

HDO can be carried out over sulphided NiMo and CoMo catalysts, which have been extensively studied in connection with hydrodesulphurisation (HDS) [2] and hydrodenitrogenation (HDN) [3]. Still, the H<sub>2</sub> activation mechanism and the active sites for hydrotreating over sulphided catalysts are not fully understood. First, H<sub>2</sub> may dissociate homolytically or heterolytically [4] and secondly, sulphided catalysts are known to have at least two types of active sites [5]. Breysse et al. [4] stated in their review dealing with H<sub>2</sub> activation that homolytic dissociation occurs mainly over a stoichiometric sulphide surface, whereas heterolytic dissociation proceeds forming a hydride and a proton over pairs of coordinatively unsaturated sites (CUS) and sulphur ions. CUS associated with MoS<sub>2</sub> phase are generally accepted to be present over the sulphided catalyst, and heterolytic dissociation of  $H_2$  is therefore the most commonly applied model. It should be added that heterolytic dissociation also describes the dissociation of  $H_2S$ .

Alumina support alone may have catalytic properties for hydrotreating reactions. Al atoms are Lewis acid sites where as the O atoms are basic sites. It is reported that  $H_2S$  may react with Al atoms but the oxygen sites are not adsorption sites for  $H_2S$ . In addition, hydroxyl groups may interact with adsorbing molecules [6]. The promoting effect of Ni or Co atoms is generally accepted to be due to an increase in the number of available vacancies. Promoter can donate electrons to Mo and lead to a weakening of the metal–sulphur bond. According to recent review by Prins [5], characterisation of supported metal sulphides is difficult, and quantitative determination of the active sites over promoted catalysts does not produce reliable results, because of the complexity of the catalyst surface.

In HDN studies, Bunch et al. [7] and Delmon [8] have proposed that hydrogenation sites are sulphur vacancies with Ni or Mo atoms and hydrogenolysis sites are Brønsted acid centres associated with Mo atoms. Detailed classification [9] suggests that the sites may have Lewis acid character referring to CUS sites, i.e., sulphur anion vacancies, and Brønsted acid character referring to SH<sup>-</sup> groups. Adsorption and dissociation of  $H_2S$  may change hydrogenation sites (CUS) to hydrogenolysis sites via formation of SH<sup>-</sup> groups [7,8]. However, it has been reported [10] that hydrogenation may occur

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<sup>0926-860</sup>X/\$ - see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2010.09.010

over Ni- and Co-promoted Mo catalysts with and without sulphur vacancies.

Density functional theory (DFT) studies have provided new insights into the structure of sulphided catalysts and the active sites for hydrogenation. Besenbacher et al. [11] summarise the latest DFT studies as follows: unpromoted and promoted MoS<sub>2</sub> catalysts have specific metallic edge sites that give rise to bright brims in scanning tunneling microscopy (STM). These edge sites could play a role in hydrogenation reactions and also in hetero-atom removal. The DFT studies indicate the weak inhibiting effect of H<sub>2</sub>S on hydrogenation reactions, since it is reported that H<sub>2</sub>S is unable to bind to the fully coordinated brim site.

Previously, we studied the HDO of phenol and methyl heptanoate over sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts [12]. Phenol was used as an aromatic model component and methyl heptanoate as an aliphatic model component for biomass-based fuels and the reactants were tested separately. Phenol was found to be less reactive than methyl heptanoate in the experiments carried out in a flow reactor at 250 °C under 1.5 MPa pressure. In some tests, H<sub>2</sub>S was added to the gas feed to maintain the activity of the sulphided catalyst. The effect of the sulphiding agent on the HDO of phenol was opposite to its effect on methyl heptanoate: the HDO conversion of phenol decreased as a function of increasing H<sub>2</sub>S concentration in the feed, whereas the HDO of the aromatic alcohol and the aliphatic ester was concluded to occur on dissimilar active sites.

Earlier studies on the HDO of mixtures [10,13,14] have been carried out with aromatic components. Clearly, however, there are differences in the behaviour of aromatic and aliphatic components over sulphided catalysts and in this study we focus on the HDO of mixtures of aromatic and aliphatic oxygen-containing model components, i.e., phenol and methyl heptanoate. The aim is to understand the reactions of aromatic and aliphatic structures over a sulphided NiMo catalyst and to derive mechanistic information that applies both to the reactants separately and in their mixtures with and without sulphur additive.

#### 2. Experimental

# 2.1. Reactor

The HDO experiments were performed in a 50 ml batch reactor (Autoclave Engineers) equipped with a fixed catalyst basket and a magnetic stirrer. The stirring rate was 1000 rpm.

# 2.2. Experiments

Commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was crushed and sieved to a fraction of 0.59–0.75 mm, dried at 100 °C for 5 h and packed (0.5 g) into the catalyst basket. The catalyst was presulphided in situ before the activity tests. At the start of the pretreatment period, the reactor was heated up to 350 °C under N<sub>2</sub> flow (atmospheric pressure), and the catalyst was dried at this temperature for 2 h. After drying, the catalyst was sulphided at 350 °C under H<sub>2</sub>S/H<sub>2</sub> (5 mol%, atmospheric pressure) flow for 2 h. Activity test temperature (200 or 250 °C) was achieved under N<sub>2</sub> flow during 30 min.

The liquid reactant solution was introduced to the preheated reactor, and the total pressure was set with  $H_2$ , typically to 7.5 MPa. The liquid added to the reactor occupied 1/3 of the reactor volume. Duration of the reaction tests varied between 1 and 5 h. The test procedure has been described in detail previously [15].

The main reactants were phenol (Fluka,  $\geq$ 99%) and methyl heptanoate (Merck, >98%) diluted with *n*-dodecane (Merck,  $\geq$ 99%). The reactions of the model components were studied both separately and as mixtures. In all tests, *n*-decane (Merck, >98%) was added as an internal standard. All gases were obtained with 99.999% purity from AGA. The effect of sulphur additive was tested in both types of experiments. The partial pressure of  $H_2S$  was adjusted with gaseous  $H_2S$  (up to 2000 ppm) or via the decomposition of a liquid sulphur component, dimethyl disulphide (0.2–0.8 wt%), DMDS (Fluka, >98%).

Compositions of the reaction mixtures (T=250 °C and P=7.5 MPa) were as follows: mixture of phenol and methyl heptanoate (both 3 wt%) was tested with H<sub>2</sub>S (650 and 2000 ppm), with DMDS (0.2, 0.4 and 0.8 wt%) and without any sulphur additives. In addition, phenol alone (3 wt%) and methyl heptanoate alone (3 wt%) were tested with DMDS (0.4 wt%) and without any sulphur additives. To determine the effect of co-reactant amount on the product distribution, lower (2 wt%) and higher (4 wt%) amounts of phenol and methyl heptanoate were also tested (keeping the amount of the other co-reactant at 3 wt% and in the absence of any sulphur additive).

Supplementary experiments were carried out with benzene (Fluka, >99.5%), cyclohexanol (Fluka,  $\geq$ 99.0%) and cyclohexene (Aldrich, 99%) to clarify the reaction pathways. These reactants were studied both individually and as reactant mixtures together with phenol.

The effect of  $H_2$  pressure was evaluated at 6.0, 7.5 and 9.0 MPa at 200 °C and with 0.4 wt% DMDS at 7.5 and 9.0 MPa at 250 °C. Temperature of 200 °C was used for three experiments to obtain a lower reaction rate and allow clarification of the initial reaction steps. In addition, the stirring rate was varied from 1000 to 1750 rpm to assess the diffusion limitations at 250 °C and 7.5 MPa.

Catalytic character of commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was explored with methyl heptanoate as a reactant. The loading of the support was 0.4 g. Pretreatment of the catalyst was similar to the one described above for NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

# 2.3. Analytical methods

Liquid samples were analysed off-line with an Agilent Technologies 7890A gas chromatograph equipped with a capillary column (HP-1,  $60 \text{ m} \times 0.25 \text{ mm} \times 1 \mu \text{m}$ ) and a flame ionisation detector. The products were quantified by internal standard method. Supplementary qualitative analyses were obtained with an Agilent Technologies 5975C mass spectrometer connected to the gas chromatograph.

# 2.4. Definitions

Calculations were carried out on the basis of the analysed liquid samples. Molar concentration of the product is the number of moles of product divided by the total number of moles, including unreacted reactant and products, and multiplied by 100%. The total amount of hydrocarbon is the sum of the products containing no hetero atoms. Hence, complete deoxygenation is achieved when the total amount of hydrocarbon is 100%.

In this work, terms phenol and methyl heptanoate refer to experiments where either of the reactants was used alone together with the solvent. Mixture, in turn, describes experiments where both phenol and methyl heptanoate, with the solvent, were used together. Some of the experiments were performed in the presence of a sulphur additive, either H<sub>2</sub>S or DMDS.

#### 3. Results

# 3.1. Reactivity in the HDO of phenol and methyl heptanoate

HDO reactions were studied at  $250 \,^{\circ}$ C over the sulphided NiMo catalyst. Using the reactant mixtures, we first tested two H<sub>2</sub> pres-



**Fig. 1.** Conversion of phenol ( $\blacklozenge$ ), methyl heptanoate ( $\blacktriangle$ ), phenol in mixture ( $\diamondsuit$ ) and methyl heptanaote in mixture ( $\bigtriangleup$ ) at 250 °C and 7.5 MPa.

sures (6.0 and 9.0 MPa), in addition to the typically used 7.5 MPa, to verify that the amount of  $H_2$  is not limiting the reactions. In addition at 250 °C and 7.5 MPa, the stirring rate was varied between 1000 and 1750 rpm at 7.5 MPa pressure. These experiments revealed neither increase nor decrease in the conversions of reactants nor changes in the product distribution. As the stirring rate was vigorous and changing the  $H_2$  pressure did not alter reactivity, there were evidently no changes in the availability of  $H_2$  due to external or internal diffusion.

Fig. 1 presents typical conversion profiles as a function of time. Complete conversion of phenol (3 wt%) and methyl heptanoate (3 wt%) at 250 °C was achieved in 150 and 80 min, respectively. Practically complete conversion of the mixture (3 wt% phenol + 3 wt% methyl heptanoate) was achieved in 240 min. The results plotted in Fig. 1 show that compared to the conversions of the components separately, conversions in the mixture decreased significantly in the case of phenol and only slightly in the case of methyl heptanoate.

# 3.2. Reactivity in the HDO of phenol and methyl heptanoate in the presence of sulphur additive

Decomposition products of DMDS are stated to vary depending on temperature [16]. Methanethiol is formed at 150°C. Increasing temperature leads to transformation of methanethiol into dimethylsulphide (DMS) and further DMS into methane and H<sub>2</sub>S. No DMDS, methanethiol or DMS was now detected and therefore, complete decomposition of DMDS to methane and H<sub>2</sub>S most probably occurred in our experimental conditions. It should also be noted that DMDS could form coke and in that case, lower the HDO reactivity compared to H<sub>2</sub>S as a sulphur additive. Texier et al. [16] have published sulphur and carbon contents of the catalyst after activation of NiMo by DMDS and H<sub>2</sub>S. When heptane was used as a solvent, the carbon contents were 0.2 wt% (with  $H_2S$ ) and 0.8 wt%(with DMDS). With 1-methylnaphthalene as solvent the carbon contents were 2.0 wt% (with H<sub>2</sub>S) and 6.5/10.0 wt% (with DMDS). Low carbon contents obtained with heptane and different sulphiding agents lets us conclude that our solvent, *n*-dodecane, is suitable for using DMDS and H<sub>2</sub>S as comparable sulphur additives.

The effect of  $H_2$  pressure on the decomposition of DMDS and on the HDO reactions was studied with the reactant mixtures at 7.5 and 9.0 MPa. As without sulphur additive, no differences in phenol and methyl heptanoate conversions or in the product distributions were observed for the two  $H_2$  pressures. These results confirmed that the reactivity of phenol and methyl heptanoate in their mixture at 7.5 MPa with DMDS is not limited by the  $H_2$  pressure.



**Fig. 2.** Effect of sulphur additive on the conversion of phenol as a function of time in mixture experiment with methyl heptanoate at  $250 \degree C$  and 7.5 MPa: no additive ( $\Diamond$ ), 0.2 wt% DMDS ( $\blacksquare$ ) and 0.4 wt% DMDS ( $\blacktriangle$ ).

The conversion of phenol in the reactant mixture experiments decreased significantly in the presence of sulphur additives as displayed in Fig. 2. No further decrease in the conversions occurred when the DMDS concentration was increased from 0.2 to 0.4 wt%. Addition of gaseous  $H_2S$  produced a similar decrease in the conversion of phenol. The conversion of methyl heptanoate with increasing concentration of  $H_2S$  or DMDS (up to 0.4 wt%) increased slightly.

## 3.3. Reaction products

# 3.3.1. Products not containing sulphur

The main products of the HDO of phenol and methyl heptanoate separately have been reported earlier [12,15]. In the case of phenol, the improved analytical system of the present study allowed the detection of a new hydrocarbon product, cyclohexyl cyclohexane, and trace amounts of two new oxygen-containing products, 2- and 4-cyclohexyl phenol. No new products were observed in the experiments with methyl heptanoate with the improved analysis. No ring opening was detected as all the products of phenol were cyclic (excluding water). Oxygen was released as water from both reactants. During the HDO of methyl heptanoate, CO and CO<sub>2</sub> were formed, too.

To clarify the formation of cyclohexyl cyclohexane, we carried out reaction tests with phenol, benzene, cyclohexanol and cyclohexene. Various reaction pathways to produce cyclohexyl cyclohexane have been proposed earlier. Tsodikov et al. [17] have reported its formation by reductive dehydration of alcohol. According to Sapre and Gates [18], however, cyclohexyl benzene can be hydrogenated to cyclohexyl cyclohexane, and several ways to produce cyclohexyl benzene have been reported [19,20]. In addition, Yadav and Kumar [21] have suggested alkylation of phenol with cyclohexene and Hong et al. [22] alkylation of phenol with cyclohexanol to produce cyclohexyl phenol. In our experiments, cylohexyl phenol as an intermediate and cyclohexyl cyclohexane as a final product was clearly produced in the presence of phenol and cyclohexene. Hydrogenation and dehydration of cyclohexyl phenol produce cyclohexyl cyclohexane. No enhanced formation of cyclohexyl cyclohexane was seen with phenol and benzene or phenol and cyclohexanol. Thus, our tests show similar reaction route for bicyclic components as Yadav and Kumar [21] have presented.

The simultaneous HDO of phenol and methyl heptanoate revealed the same main products as in the single component tests. Yet, the main products were present in different ratios, and trace amounts (not more than 2 mol%) of several new products were detected: methyl cyclohexane, methoxy benzene, 2- and 3methyl phenol, phenyl heptanoate and 4-heptyl phenol. These new oxygen-containing components were formed because of the simultaneous presence of phenol and methyl heptanoate. All the oxygenand sulphur-containing products were classified as intermediates, because they were not observed at complete conversion.

To determine the effect of reactants on the product distribution, the amount of phenol was varied while the amount of methyl heptanoate was held constant, and vice versa. At complete deoxygenation, molar concentrations of cyclic and aliphatic hydrocarbons consistently reached the same amounts as were used in the reactant solutions. For example, in the solution of phenol and methyl heptanoate (3 wt%: 3 wt%, 60 mol%: 40 mol%), cyclic products comprised 60 mol% and aliphatic products 40 mol%. Only trace amounts of combined products were formed during the reaction and since they were intermediates they did not affect the amounts of cyclic and aliphatic products at the point of complete deoxygenation.

The experiment with sulphided  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and methyl heptanoate showed low production of heptanoic acid and methanol. No hydrocarbons were detected. Between 60 and 90 min the conversion of methyl heptanoate was unchanged at 16%. For comparison, the conversion with sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 100% at 90 min [15].

#### 3.3.2. Sulphur-containing products

Trace amounts of sulphur-containing products were observed in the experiments without sulphur additive. Formation of sulphurcontaining components in the HDO of methyl heptanoate without sulphur additive was earlier reported [15] to take place in the reaction mixture because sulphur that was attached to the catalyst surface during pretreatment reacted with various intermediates. Sulphur content of the catalyst on carbon free basis has not been observed to vary in batch reactor experiments. Using methyl heptanoate as a reactant without sulphur additive, the sulphur content was 5.7 wt% before HDO experiment and 5.6 wt% after [15].

Two sulphiding agents, DMDS and  $H_2S$ , were used to study the effect of sulphur additive on the HDO of phenol and methyl heptanoate separately and in reactant mixtures. Sulphur-containing products in the methyl heptanoate experiments were identified as methanethiol, heptanethiol, hexanethiol, dimethyl sulphide and diheptyl sulphide. In the phenol experiments, only cyclo-hexanethiol was detected. In the mixture experiments, all the above-mentioned products plus 1- and 2-methyl thioheptane were detected. The products were the same independent of the sulphur additive. The total amounts of the sulphur-containing components with and without added DMDS are shown in Fig. 3 as a function of the progress of deoxygenation. The greater the sulphur addition, the more sulphur components were formed. Similarly, the total amount of the sulphur components increased as a function of increasing  $H_2S$  concentration.

# 3.4. Hydrocarbon distribution

The differences in the distributions of the main hydrocarbon products (cyclohexane, cyclohexyl cyclohexane, heptane and hexane) between the experiments with phenol and methyl heptanoate separately and with their mixtures can be compared in terms of the molar concentrations of these products without sulphur additive. In the presentation of mixture results, cyclic products of phenol and aliphatic products of methyl heptanoate are calculated separately. Concentration profiles for cyclohexane and cyclohexyl cyclohexane are shown in Fig. 4a and those for heptane and hexane in Fig. 4b. Amounts of cyclohexene, benzene, methyl cyclohexane, hexenes and heptenes were low and are not shown in the figures.

Further comparisons of the results can be carried out at complete deoxygenation. The fractions of cyclohexane and cyclohexyl

**Fig. 3.** Total amount of sulphur-containing compounds formed in HDO of phenol and methyl heptanaote mixture with increasing fraction of sulphur additive at 250 °C and 7.5 MPa: no additive ( $\Diamond$ ), 0.2 wt% DMDS ( $\blacksquare$ ), 0.4 wt% DMDS ( $\blacktriangle$ ) and 0.8 wt% DMDS (-).

cyclohexane in the experiments with phenol and with the reactant mixture are shown in Fig. 5. The group designated "others" consisted of benzene in the phenol experiments and of benzene and methyl cyclohexane in the mixture experiments. Comparison of the molar concentrations shows that, in the case of the reactant mixture, the fraction of cyclohexane increased and that of cyclohexyl cyclohexane decreased relative to the experiment with phenol alone. Fig. 5 also shows the hydrocarbon distribution at complete deoxygenation for methyl heptanoate and for methyl heptanoate in the mixture. A shift towards  $C_6$  hydrocarbons occurred when phenol was present.



**Fig. 4.** (a) Concentration profiles of cyclohexane ( $\blacktriangle$ ) and cyclohexyl cyclohexane (-) in HDO of phenol and methyl heptanoate mixture at 250 °C and 7.5 MPa. (b) Concentration profiles of heptane ( $\blacksquare$ ) and hexane ( $\blacklozenge$ ) in HDO of phenol and methyl heptanoate mixture at 250 °C and 7.5 MPa.



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# Table 1

Ratios for products of phenol (monocyclic and bicyclic components) and methyl heptanoate (heptenes, heptane, hexenes and hexane) in the HDO of phenol and methyl heptanoate and of their mixture at total hydrocarbon amount of 50%.

	Monocyclics/bicyclic		(Heptenes + heptane)/(hexenes + hexane)	
	No sulphur additive	0.4 wt% DMDS	No sulphur additive	0.4 wt% DMDS
Reactant alone (3 wt%)	11.5	4.6	5.3	4.0
Mixture (3 wt%+3 wt%)	24.0	11.5	2.8	3.2



**Fig. 5.** Molar concentrations of cyclic and aliphatic hydrocarbon products at complete deoxygenation of phenol and methyl heptanoate and of their mixture at 250 °C and 7.5 MPa: cyclohexane (black), cyclohexyl cyclohexane (grey) and "others" including benzene in phenol alone and both benzene and methyl cyclohexane in mixture (white), heptane (horizontal lines) and hexane (dots).

### 3.5. Hydrocarbon distribution in the presence of sulphur additive

Product distributions at the hydrocarbon amount of 50 mol% are displayed in Fig. 6a and b for phenol and methyl heptanoate separately and in their mixture, with and without sulphur additive (DMDS 0.4 wt%). At this point the yield of deoxygenated products is half of their final amount. Table 1 shows the ratios of monocyclic (cyclohexane and cyclohexene) to bicyclic (cyclohexyl cyclohexane) components and of C<sub>7</sub> (heptane and heptenes) to C<sub>6</sub> (hexane and hexenes) components calculated from details of Fig. 6a and b. These results depict points at different reactant conversions because the addition of sulphur affects the conversions. For comparison, the product distribution values at around 20% phenol conversion in mixture experiments are reported in Tables 2a and 2b. Product distribution with 0.2 wt% DMDS is listed, too. To enable analysis of phenol and methyl heptanoate experiments at comparable points the methyl heptanoate conversions are different.

When sulphur was added, the ratio of monocyclic to bicyclic components decreased in a similar way in the experiments with phenol (from 11.5 to 4.6) and in those with the mixture (from 24.0 to 11.5)(Table 1). In the experiments with methyl heptanoate, however, the ratio of  $C_7$  to  $C_6$  decreased from 5.3 to 4.0 with added

#### Table 2a

Product distribution (mol%) of HDO of phenol in mixture with methyl heptanoate in the absence and presence of sulphur at around 20% phenol conversion.

	No sulphur additive	0.2 wt% DMDS	0.4 wt% DMDS
Cyclohexene	0.7	0.7	0.4
Cyclohexane	2.4	0.6	0.3
Cyclohexyl cyclohexane	0.0	0.0	0.0
Benzene	0.1	0.0	0.0
Methyl cyclohexane	0.0	0.0	0.0
Oxygen-containing cyclic intermediates	4.4	4.1	4.0
Sulphur-containing cyclic intermediates	0.02	0.2	0.2
Unreacted phenol	92.4	94.4	95.1



**Fig. 6.** (a) Product distributions in the HDO of phenol alone (phenol), phenol in mixture with methyl heptanoate (mixture/phenol), phenol alone with sulphur additive (phenol+S) and phenol in mixture with methyl heptanoate and sulphur (mixture/phenol+S) at total hydrocarbon amount of 50 mol% at 250 °C and 7.5 MPa: cyclohexane (dots), cyclohexene (white), cyclohexyl cyclohexane (grey) and cyclic intermediates (black). (b) Product distribution in the HDO of methyl heptanoate alone (MH), methyl heptanoate in mixture with phenol (mixture/MH), methyl heptanoate alone with sulphur additive (MH+S) and methyl heptanoate in mixture with phenol and sulphur (mixture/MH+S) at total hydrocarbon amount of 50 mol% at 250 °C and 7.5 MPa: heptane (horizontal lines), heptenes (dots), hexane (white), hexenes (grey) and aliphatic intermediates (black).

#### Table 2b

Product distribution (mol%) of HDO of methyl heptanoate in mixture with phenol in the absence and presence of sulphur at around 20% phenol conversion.

	No sulphur additive	0.2 wt% DMDS	0.4 wt% DMDS
Hexenes	1.4	4.1	5.2
Hexane	9.2	6.4	4.6
Heptenes	4.0	15.9	17.4
Heptane	20.9	22.1	15.0
Oxygen-containing aliphatic intermediates	33.7	26.5	23.6
Sulphur-containing aliphatic intermediates	0.2	5.1	11.2
Unreacted methyl heptanoate	30.6	19.9	23.0

sulphur indicating a decrease in the amount of  $C_7$  hydrocarbons but no apparent change in the ratio of  $C_7$  to  $C_6$  occurred in the mixture experiments (increase from 2.8 to 3.2). In general, the changes due to the sulphur additive were more pronounced for phenol. In the experiments with methyl heptanoate (Fig. 6b and Table 2b) sulphur caused an increase in the molar concentrations of heptenes and hexenes.

### 4. Discussion

# 4.1. Steps involved in the HDO of phenol and methyl heptanoate

The main end products in the simultaneous HDO of phenol and methyl heptanoate were cyclohexane, cyclohexyl cyclohexane, hexane and heptane (Fig. 4a and b). Methyl cyclohexane was also formed, but its molar concentration at complete deoxygenation was only 2 mol%.

The most often used classification of hydrotreating into hydrogenolysis and hydrogenation is not adequate in the HDO of phenol and methyl heptanoate since the acid-catalysed reactions cannot be combined with either the hydrogenolysis or the hydrogenation reactions. In this work, we instead divide the reactions into the following categories:

# (1) reductive reactions, where

- a. H<sub>2</sub> is added, i.e., hydrogenation (saturation of double-bond) or
- b. H<sub>2</sub> is added and simultaneously water or alcohol is released (hydrogen is added adjacent to carbonyl carbon)
- (2) acid-catalysed reactions refer to esterification, hydrolysis, dehydration and alkylation (initiated with electrophilic proton transfer to nucleophilic oxygen of the reacting molecule)
- (3) decarbonylation reactions (removal of carbon monoxide)

Reaction steps in the HDO of phenol [12] are mainly reductive (Scheme 1). Reactions of phenol, benzene, cyclohexanone and cyclohexene to cyclohexane belong to this group as do reactions from cyclohexyl phenol to cyclohexyl cyclohexane. Dehydration of cyclohexanol to cyclohexene and alkylation of phenol with cyclohexene, on the other hand, are acid-catalysed reactions.

The reaction steps in the HDO of methyl heptanoate [23] (Scheme 2) include the decarbonylation reactions of heptanoic acid and heptanal and acid-catalysed reactions, which are methyl heptanoate hydrolysis, heptanol dehydration and esterification of heptanoic acid with heptanol. Reduction reactions include steps from ester to heptanol, from heptanoic acid to heptanal, from heptanal to heptanol and from hexenes and heptenes to hexane and heptane. Methyl heptanoate may also react through alkaline hydrolysis [15] with SH<sup>-</sup> or OH<sup>-</sup> nucleophiles.



Scheme 1. Reaction pathways of the HDO reactions of phenol over sulphided catalyst [12].

#### 4.2. Reaction pathways without sulphur additive

Reactivity tests for phenol and methyl heptanoate separately and for their mixtures without sulphur additive indicated that phenol was more sensitive to the presence of the other reactant than methyl heptanoate was (Fig. 1). The hindering effect of methyl heptanoate on the reactivity of phenol indicates that some of the reaction steps of the reactants or their intermediates are competing for the same active sites of the catalyst.

The alkylation of phenol with cyclohexene requires the protonation of cyclohexene, and protonation of cyclohexene most likely occurs on acidic sites. The differences in the product distributions presented in Fig. 5 suggest that acid-catalysed alkylation of phenol is suppressed in the reactant mixture experiments. In addition, the fact that the conversion of methyl heptanoate was practically unchanged in the presence of co-reactant (Fig. 1) indicates that the reactivity of methyl heptanoate was only slightly affected by the reactions of phenol. It seems likely, therefore, that methyl heptanoate or its intermediates capture the active sites for their acid-catalysed reactions.

In addition to the product concentrations of phenol, those of methyl heptanoate changed in the presence of co-reactant (Fig. 5). The molar concentration of  $C_6$  hydrocarbons increased from 9 (reactant alone) to 15 mol% (mixture) although  $C_7$  hydrocarbons still were the main components.

We have previously [15] shown that the reduction of methyl heptanoate is only a minor route to heptanol. Here, therefore, our discussion of the formation of  $C_7$  hydrocarbons focuses on the reductive reactions of heptanoic acid and heptanal. We also previously [15] concluded that the production of  $C_6$  hydrocarbons by decarbonylation occurred predominantly from heptanoic acid. Hence, the increase in  $C_6$  molar concentration in the mixture may



Scheme 2. Reaction pathways of the HDO reactions of methyl heptanoate over sulphided catalyst [23].

be explained by suppression of the reduction of heptanoic acid and heptanal due to the competitive adsorption of acid or aldehyde and phenol or intermediates on the same active sites.

# 4.3. Reaction pathways with sulphur additive

When sulphur was added to the mixture of reactants the conversion of phenol was lower as a function of time (Fig. 2) compared to the experiment without sulphur. In contrast, the conversion of methyl heptanoate increased slightly compared to the experiment without sulphur. Earlier [12], in the experiments where phenol and methyl heptanoate were studied separately in a flow reactor H<sub>2</sub>S had a similar suppressing effect on the reactivity of phenol but clearly promoting effect on methyl heptanoate conversion. The fact that the flow reactor studies were carried out in gas phase may have contributed to the difference in the results. Here we compare only the results obtained with DMDS, because the changes are clearer. In the case of product distributions sulphur addition had a weaker effect in the experiments with methyl heptanoate than in those with phenol (Tables 1, 2a and 2b). The more sulphur was added to the reactant mixtures the larger was the fraction of sulphur-containing intermediates (Fig. 3, Tables 2a and 2b).

Product distributions at the hydrocarbon amount of 50 mol% are displayed in Fig. 6a and b for phenol and methyl heptanoate separately and in their mixture, with and without sulphur additive (DMDS 0.4 wt%). At this point 50 mol% of the liquid components in the system are totally deoxygenated. In the case of methyl heptanoate alone, the route to C7 hydrocarbons was slightly suppressed when sulphur was added. Comparison of methyl heptanoate alone and in the reactant mixture revealed suppression in route to  $C_7$ . However, no additional suppression of this route to  $C_7$  was observed in the reactant mixture with sulphur additive. These results indicate that phenol, or its intermediates, and sulphur have the same hindering effect on acid and aldehyde reduction. Related to this Wang et al. [24] have reported that the competitive adsorption of aldehyde and sulphur species suppresses the reduction of aldehyde because sulphur decreases the number of active sites available for the reactions of aldehyde.

In the case of phenol, sulphur addition decreased the fraction of cyclohexane indicating hindering effect of sulphur on the hydrogenation of benzene and cyclohexene (Fig. 6a). Moderate decrease in the fraction of monocyclics was also observed in the reactant mixture with sulphur. Sulphur addition in methyl heptanoate experiments increased the fractions of hexenes and heptenes, again because of hindering of hydrogenation reactions. A recent publication [25] on the impact of H<sub>2</sub>S on the reactivity of 1-hexene over CoMo catalyst suggests that sulphur components are adsorbed on the same site where alkenes are saturated. Our observation that sulphur additive (here DMDS) decreases the fraction of cyclohexane is in good agreement with this. Probably alkene adsorption is hindered and, further, the hydrogenation reactions.

#### 4.4. Catalyst surface and reactivity relations

For further consideration of the role of specific active sites, it is useful to explore the reacting components (phenol, methyl heptanoate and sulphur) and the reaction types (reduction, acid-catalysed reactions and decarbonylation). Earlier studies of our group [26] showed that acid-catalysed reactions occur on sulphur-saturated sites. Since methyl heptanoate hydrolysis is an acid-catalysed reaction, it occurs on a sulphur-saturated site. It has also been found [7,8] that CUS can be transformed to sulphur-saturated sites in the presence of H<sub>2</sub>S, and the acidity of the catalyst is thereby increased. Our study clearly shows that sulphur additive affects phenol and methyl heptanoate dissimilarly, in particular by suppressing the reactivity of phenol. On the basis of this finding

it seems probable that phenol and methyl heptanoate adsorb on different active sites, and we propose that phenol adsorbs on CUS. As described above, suppressed reduction of heptanoic acid and heptanal due to competitive adsorption of phenol or its intermediates suggests that these reactions also occur on CUS. Moreover, since sulphur additive hinders hydrogenation, we can presume that hydrogenation, too, occurs on CUS. We may further extend our conclusions to state that all the reduction reactions occur on CUS and compete with the adsorption of sulphur.

Kasztelan and Guillaume [27] carried out extensive studies on the inhibiting effect of  $H_2S$  on toluene hydrogenation over unpromoted MoS<sub>2</sub> catalyst and reported that hydrogenation proceeds by addition of hydride to toluene followed by addition of proton, or vice versa. Heterolytically dissociated  $H_2$ , indeed, provide hydrides and protons on CUS [4]. Thus, inhibition of reduction (hydrogenation) in the presence of sulphur additive may be partly due to decrease in CUS but partly also in the availability of hydrides. Our earlier [15] conclusion that protonic SH<sup>-</sup> groups (sulphursaturated sites) serve as a hydrogen source is still valid because these species may release protons for reactions occurring on both CUS and sulphur-saturated site.

As presented in Scheme 2, heptanoic acid may react further by reduction, decarbonylation and esterification. In this study it is proposed that reduction occurs on CUS and the acid-catalysed esterification on sulphur-saturated sites. The site for decarbonylation cannot be exclusively assigned on the basis of our reaction data. Probably, however, decarbonylation occurs on sulphur-saturated sites because, in the presence of sulphur additive, the suppression of acid/aldehyde reduction increased the fraction of C<sub>6</sub> hydrocarbons. If instead decarbonylation had occurred on CUS, formation of C<sub>6</sub> hydrocarbons would have been suppressed, too, and the reactivity of methyl heptanoate and its intermediates would have decreased relative to tests without the sulphur additive.

We earlier [15] concluded that the high nucleophilic strength of SH<sup>-</sup> groups is important in the hydrodeoxygenation reactions of aliphatic esters. Depending on the sulphidation state of the catalyst, the surface of the catalyst also contains OH<sup>-</sup> groups, whose action is similar to but weaker than that of the SH<sup>-</sup> groups. Therefore, the ratio of CUS and sulphur-saturated sites is not the only determining factor in the reactivity.

In our test, alumina was found to slightly catalyse the formation of heptanoic acid and methanol from methyl heptanoate. Sulphidation of alumina is reported to increase the Brønsted acidity [28] and thus enhance the acid-catalysed reactions such as ester hydrolysis. The reaction between heptanoic acid and heptanal was not observed which shows that reactions taking place on CUS cannot probably occur on alumina. As a conclusion, sulphided alumina has potential to catalyse acid-catalysed reactions but not reduction reactions and NiMoS structure is needed to enhance the reactivity.

## 5. Conclusions

The present study deals with the HDO of phenol and methyl heptanoate over sulphided NiMo catalyst. Conversion of phenol decreased in a reactant mixture. At complete deoxygenation of the mixture, the fraction of cyclohexane was increased relative to the fraction obtained with phenol alone. This result was explained by suppression of the acid-catalysed alkylation of phenol by the dominating acid-catalysed reactions of methyl heptanoate. Although phenol had only a minor effect on the total conversion of methyl heptanoate, it had a suppressing effect on the reaction pathway from methyl heptanoate to C<sub>7</sub> hydrocarbons. The reduction of heptanoic acid or heptanal or both was also hindered, most probably because of competition with the reduction reactions of phenol.

In the reactant mixture, sulphur had a weaker effect on the reactions of methyl heptanoate than on those of phenol. Sulphur suppressed the conversion of phenol and the molar concentration of bicyclic components decreased, but conversion and product distribution of methyl heptanoate remained practically unchanged. Contrary to the finding in the reactant mixture, when sulphur was added to the methyl heptanoate alone, the amount of C<sub>7</sub> hydrocarbons decreased. In the mixture, therefore, cyclic components and sulphur have the same hindering effect on the reduction of heptanoic acid and aldehyde, and sulphur has no additional effect on the reduction reactions. In addition, sulphur decreases the hydrogenation of alkenes.

On the basis of the experiments carried out with the reactant mixture as well as with sulphur additive, we conclude that reduction reactions (including hydrogenation) occur on CUS. Sulphur-saturated sites, in turn, are needed for acid-catalysed and decarbonylation reactions. In addition, sulphur adsorbs on CUS and affects the reactions occurring on these sites.

#### Acknowledgements

The authors thank Prof. Reija Jokela for valuable discussions and Mr. Kari Valkama for performing part of the experimental work. Dr. Maija Honkela received support from the Academy of Finland through Postdoctoral Researcher's Project No 115221.

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