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# Effect of sulphiding agents on the hydrodeoxygenation of aliphatic esters on sulphided catalysts

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## Abstract

In hydrodeoxygenation (HDO) on sulphided hydrotreating catalysts, addition of a sulphiding agent is typically required to maintain the catalyst activity. The effects of H<sub>2</sub>S and CS<sub>2</sub> on the HDO of aliphatic esters on sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were investigated in a fixed-bed flow reactor. The model compounds studied were methyl heptanoate, ethyl heptanoate, heptanol and heptanoic acid. The HDO produced C<sub>7</sub> and C<sub>6</sub> hydrocarbons in reactions where oxygen- and sulphur-containing compounds were formed as intermediates. Unlike CS<sub>2</sub>, H<sub>2</sub>S had a promoting effect on the HDO of the aliphatic oxygenates. The addition of H<sub>2</sub>S stabilised the selectivities as a function of time, and shifted the main products from C<sub>7</sub> to C<sub>6</sub> hydrocarbons, but did not prevent catalyst deactivation. The promoting effect of H<sub>2</sub>S was attributed to the increased catalyst acidity, which enhanced the acid-catalysed reactions (hydrolysis, esterification, dehydration, E<sub>2</sub> elimination and S<sub>N</sub>2 nucleophilic substitution). Both H<sub>2</sub>S and CS<sub>2</sub> suppressed the hydrogenation reactions on the NiMo catalyst but did not affect them significantly on the CoMo catalyst. H<sub>2</sub>S induced less hydrogen consumption and coke formation than CS<sub>2</sub>, but the carbon efficiency suffered in the presence of H<sub>2</sub>S. Thus, the use of H<sub>2</sub>S as sulphiding agent in the HDO of the aliphatic oxygenates was concluded to be more beneficial than the use of CS<sub>2</sub>. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Bio-oil; Hydrodeoxygenation; Sulphided catalyst; Hydrogen sulphide; Carbon disulphide; Aliphatic ester

## 1. Introduction

The transportation sector accounts for more than 30% of the energy consumption in the European Union, and consumption is continuously increasing [1]. The EU is calling for partial substitution of biomass-based alternatives for fossil fuels [1] and, in recent years, much effort has been invested in the development of technologies for their production.

Wood-based biomass is one renewable alternative for the production of transport fuels [1–3]. The crude from pyrolysis and liquefaction of wood-based biomass, known as bio-oil, contains various oxygen functionalities, such as carboxyl, carbonyl, hydroxyl and methoxy groups, depending on the biomass origin and the production conditions [2,4,5]. In addition, water is present in large amounts (15–30 wt%) [6,7]. The total oxygen content of bio-oils may thus be as much as 50 wt% [2,4]. Because of the deleterious effects of high oxygen

content on fuel properties such as thermal and chemical stability and miscibility with hydrocarbons, bio-oils must be upgraded. The oxygen content must be reduced [2,3].

The upgrading can be achieved by hydrodeoxygenation (HDO), which involves hydroprocessing on hydrotreating catalysts similar to those used for hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN) in oil refineries [4]. The catalysts are much more active in their sulphided form, and the oxygen content of the feed has a deleterious effect on the sulphide structure of the catalysts causing losses in activity and changes in product distribution [4]. Since the sulphur content of bio-oils is typically very low, addition of a sulphiding agent to the feed seems to be a reasonable means of maintaining the catalyst in its sulphided state [4,8,9]. The effect of sulphiding agents has, however, been shown to vary with the type of catalyst and composition of the feedstock [4]. Sulphiding agents have been reported to suppress the HDO of phenols [10–12] and the HDS of dibenzothiophenes [13–17] on sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. Moreover, the addition of H<sub>2</sub>S reportedly suppresses the activity of sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of ketonic groups, but

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has no effect on the activity of sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst [18]. On both catalysts, H<sub>2</sub>S has an enhancing effect on the conversion of the carboxylic group of esters and no effect on the removal of the methoxy group of guaiacol [18]. The different results indicate the need for a detailed investigation of the advantages and disadvantages of various sulphiding compounds in HDO of different oxygenates present in bio-oils. Only then can a full understanding and reliable optimisation of the upgrading process conditions be obtained.

Recently, we studied the reactions of aliphatic esters on sulphided catalysts [19,20]. We observed that, in the absence of a sulphiding agent, the catalysts deactivated, and the selectivities to different hydrocarbons changed with time. Water inhibited the reactions, but its presence cannot be avoided since it is formed during HDO. The addition of H<sub>2</sub>S compensated the inhibition by water, but also changed the product distribution. The present study comprises a detailed investigation of the effect of sulphiding agents on the HDO of aliphatic esters. For this purpose, experiments with aliphatic methyl ester, ethyl ester, alcohol and carboxylic acid were performed in the presence of sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts with H<sub>2</sub>S added to the feed at various concentrations. In order to clarify the effects, additional experiments with the methyl ester were carried out in the presence of CS<sub>2</sub>. Potential catalytic sites are discussed on the basis of the obtained data.

## 2. Experimental

### 2.1. Catalytic runs

Commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> hydrotreating catalysts were crushed and sieved to a fraction of 0.59–0.75 mm. The catalyst (0.5 g) was packed between two layers of silicon carbide (1–3 mm) in a stainless steel tubular fixed-bed flow reactor (i.d. 10 mm, length 380 mm) and activated as described in a previous study [20].

Experiments were carried out isothermally at 250 °C under 1.5 MPa pressure. Either 0.25 or 5 vol% H<sub>2</sub>S/H<sub>2</sub> mixture (AGA, 99.999%) was blended with hydrogen (AGA, 99.999%) feed at various flow rates to obtain 140, 500 or 1000 ppm H<sub>2</sub>S in molar basis in the reactor. An additional run with the NiMo catalyst was carried out by adding a very high H<sub>2</sub>S concentration of 24,000 ppm in molar basis. The total gas flow rate in all experiments was set to 2 l/h (NTP). The liquid mixture of 3 wt% methyl heptanoate (Fluka Chemika, >99%) or ethyl heptanoate (Aldrich, 99%) in *m*-xylene (Fluka Chemika, >98%) was fed at a rate of 10 g/h. When the effect of CS<sub>2</sub> was studied, experiments were performed by adding CS<sub>2</sub> (Merck, >99.7%) to a liquid feed that contained 3 wt% methyl heptanoate. The concentration of CS<sub>2</sub> in the reactor was calculated to be 740, 2200 or 3700 ppm in molar basis. Liquid samples were taken from the sampling vessel after a 2 h stabilisation period, and the sampling was repeated every 30 min. A standard run was continued for 6.5 h. The thermodynamic calculations indicated that, under the studied conditions, the reactant and products are all in gas phase.

To clarify the effect of H<sub>2</sub>S on the reactions, additional experiments were performed in the presence of H<sub>2</sub>S with 1-heptanol (Aldrich, 98%) and *n*-heptanoic acid (Aldrich, 99%), which were formed as intermediates in the reactions of the esters [19,20]. The results were compared with those obtained under the same conditions but in the absence of H<sub>2</sub>S [19]. Experiments with heptanoic acid were carried out with 0.5 g catalyst loading and 3 wt% acid in *m*-xylene. The concentration of H<sub>2</sub>S in the reactor was either 250 or 1675 ppm. In the experiments with heptanol, the amounts of catalyst and reactant were chosen differently from those used in the experiments with the acid due to high reactivity of the alcohol. The amounts of the NiMo and CoMo catalysts were 0.2 and 0.3 g, respectively. Heptanol contents of the liquid feed were 15 wt% when the NiMo catalyst was used and 6 wt% when the CoMo catalyst was used. The concentration of H<sub>2</sub>S in the reactor was either 4500 or 7000 ppm in different runs.

### 2.2. Analyses

The liquid samples were analysed with a gas chromatograph (HP 6890 Series) equipped with an HP-1 column (60 m × 0.25 mm and 1 μm film thickness) and a flame ionisation detector. A few samples from different experiments were analysed qualitatively with a GC/MS for product identification. The gas outlet stream was qualitatively analysed with an online gas chromatograph (HP 5890A, thermal conductivity detector, HP-PLOT/U column with dimensions 30 m × 0.32 mm and 10 μm film thickness).

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

### 2.3. Definitions

Conversions, selectivities and yields were calculated in molar basis. The total conversion was defined as the ratio of the converted reactant to the reactant fed, and the HDO conversion as the fraction of the reactant converted to hydrocarbons. The selectivity was equal to the ratio of a product to the converted reactant, and the reaction yield was calculated as the product of the total conversion and the selectivity on a per cent basis.

## 3. Results

Comparison of conversions and hydrocarbon yields from repeated experiments revealed that the experiments were well reproducible: the conversion values and hydrocarbon yields fell within ±2 percentage units. Molar balances based on analysis of the liquid product averaged over 95%.

### 3.1. Catalyst activities

#### 3.1.1. Stability of catalysts

The total ester conversion in the absence of sulphiding agents was previously found to reach a pseudo steady-state after

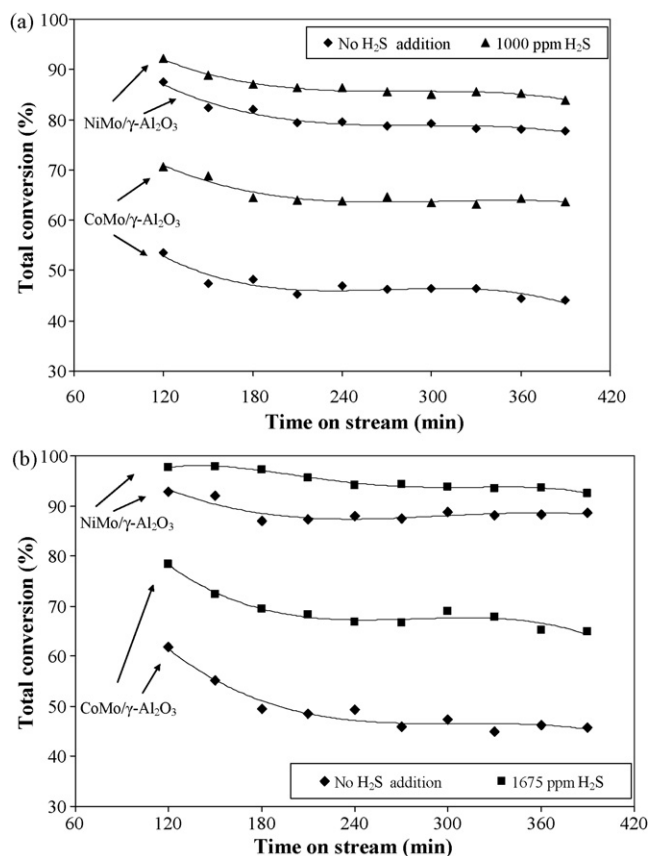


Fig. 1. Effect of H<sub>2</sub>S on the total conversion of (a) methyl heptanoate and (b) heptanoic acid on the sulphided catalysts as a function of time.

a sharp decrease (about 10 percentage units) in the first 4 h [19]. Similar behaviour was observed in this work in the presence of sulphiding agents, particularly in the total ester and acid conversions, as seen in Fig. 1. Accordingly, later in this paper, conversions, selectivities and yields are compared with the average values calculated after a pseudo steady-state was reached (usually between 4 and 6.5 h).

Before the reactions, the sulphur content of both presulphided catalysts was  $7.0 \pm 0.3$  wt%. In the absence of sulphiding agent, the carbon-free sulphur contents of the catalysts decreased during the reactions of the esters, as

Table 2

Effect of H<sub>2</sub>S on the total and HDO conversions of 1-heptanol and *n*-heptanoic acid on sulphided catalysts

H <sub>2</sub> S (ppm)	1-Heptanol <sup>a</sup>			<i>n</i> -Heptanoic acid <sup>b</sup>		
	0 <sup>c</sup>	4500	7000	0 <sup>c</sup>	250	1675
NiMo/γ-Al <sub>2</sub> O <sub>3</sub>						
Total conversion (%)	56	59	62	88	86	94
HDO conversion (%)	49	54	56	82	81	93
CoMo/γ-Al <sub>2</sub> O <sub>3</sub>						
Total conversion (%)	82	91	93	47	51	67
HDO conversion (%)	75	89	90	34	44	65

<sup>a</sup> Reaction products detected in liquid samples included C<sub>7</sub> hydrocarbons, diheptyl ether, 1-heptanethiol and diheptyl sulphide.

<sup>b</sup> Reaction products detected in liquid samples included C<sub>6</sub> and C<sub>7</sub> hydrocarbons, 1-heptanol, heptyl heptanoate, heptanal, diheptyl ether, 1-hexanethiol and 1-heptanethiol.

<sup>c</sup> From Ref. [19].

seen in Table 1. With the addition of sulphiding agent, regardless of the amount in the feed, the sulphur content of the NiMo catalysts was nearly maintained, but that of the CoMo catalyst still decreased (Table 1). The sulphur contents of the catalysts changed in a similar way in the reactions of heptanol and heptanoic acid as in the reactions of the esters.

In all experiments, carbon deposited on the catalysts during the reactions (Table 1). No correlation was found between the carbon content and the concentration of H<sub>2</sub>S in the feed. However, comparison of the carbon contents in the presence of H<sub>2</sub>S and CS<sub>2</sub> revealed greater carbon deposition in the presence of CS<sub>2</sub> (Table 1).

### 3.1.2. Effects of H<sub>2</sub>S and CS<sub>2</sub> on catalyst activities

On both catalysts, the total ester conversions increased with the concentration of H<sub>2</sub>S in the feed, as seen in Fig. 2. The HDO conversions increased as well. With the addition of 1000 ppm H<sub>2</sub>S, for example, the HDO conversion of methyl heptanoate increased from 67 to 76% on the NiMo catalyst and from 34 to 55% on the CoMo catalyst. In the reactions of ethyl heptanoate, the increase in the HDO conversion was from 63 to 83% on the NiMo catalyst and from 37 to 65% on the CoMo catalyst.

Table 1

Sulphur and carbon contents of the catalysts used in reactions of esters after 6.5 h on stream

	Methyl heptanoate					Ethyl heptanoate					
	H <sub>2</sub> S (ppm)					CS <sub>2</sub> (ppm)			H <sub>2</sub> S (ppm)		
	0 <sup>a</sup>	140	500	1000 <sup>b</sup>	24,000	740	2200	3700	0	140	1000
NiMo/γ-Al <sub>2</sub> O <sub>3</sub>											
Sulphur (wt%) <sup>c</sup>	6.0	6.9	7.0	6.9	6.7	7.0	7.1	7.0	6.1	7.1	6.9
Carbon (wt%)	6.2	6.0	6.2	5.8	4.9	7.0	7.1	7.0	6.1	5.1	6.2
CoMo/γ-Al <sub>2</sub> O <sub>3</sub>											
Sulphur (wt%) <sup>c</sup>	5.4	5.4	5.6	5.8	–	5.7	5.8	5.8	5.2	6.2	5.8
Carbon (wt%)	7.5	5.9	6.2	6.5	–	6.9	7.0	7.1	6.2	6.1	6.4

<sup>a</sup> From Ref. [19].

<sup>b</sup> From Ref. [20].

<sup>c</sup> Sulphur content of the catalyst on carbon-free basis ( $7.0 \pm 0.3$  wt% before the reactions).

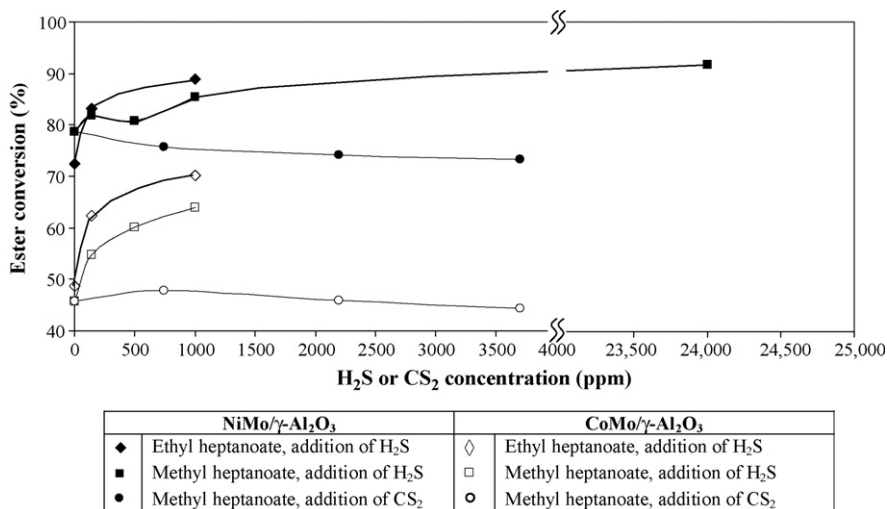


Fig. 2. Effects of addition of H<sub>2</sub>S and CS<sub>2</sub> on the total conversions of methyl and ethyl heptanoate on the sulphided catalysts.

Likewise, the addition of H<sub>2</sub>S improved the total and HDO conversions of heptanol and heptanoic acid, as shown in Table 2.

The addition of CS<sub>2</sub>, regardless of the amount, did not alter the total ester conversion noticeably (Fig. 2), and it decreased the HDO conversion. The addition of 3700 ppm CS<sub>2</sub>, for instance, decreased the HDO conversion of the methyl ester from 67 to 44% on the NiMo catalyst and from 34 to 19% on the CoMo catalyst.

### 3.2. Product distribution

The reaction products detected in the liquid samples in both absence and presence of the sulphiding agents were hydrocarbons, and oxygen- and sulphur-containing compounds, as shown in Table 3. The analysis of the gas outlet stream revealed the formation of carbon oxides (CO<sub>2</sub> and CO) in the reactions of the esters and the acid. In addition, methane and ethane were detected in the reactions of methyl heptanoate and ethyl heptanoate, respectively. No gaseous product was found in the reactions of heptanol.

The reaction products of the esters in the liquid samples were mainly hydrocarbons, heptanol, heptanoic acid and heptyl heptanoate. Total selectivity to the other oxygen-containing compounds never exceeded 3%, and sulphur-containing compounds were formed in trace amounts.

#### 3.2.1. Effect of H<sub>2</sub>S on product distribution

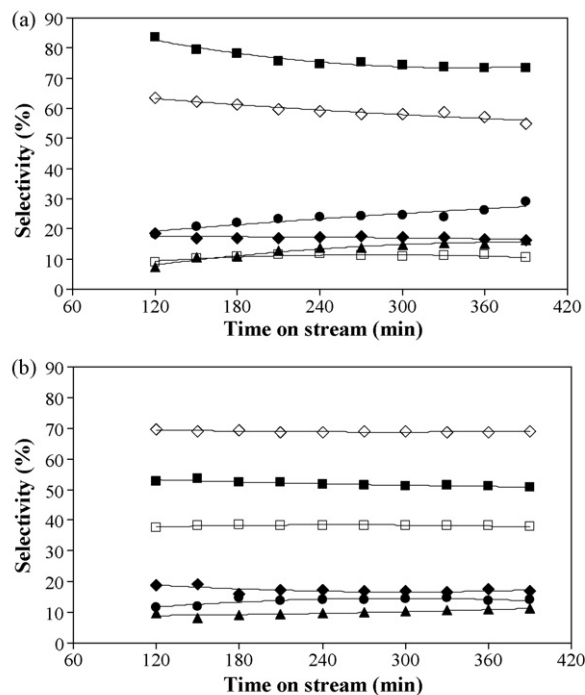
In the absence of H<sub>2</sub>S, on both catalysts, the selectivities to hydrocarbons changed as a function of time. For instance, product selectivities changed as a function of time during the HDO of methyl heptanoate in the absence and presence of 1000 ppm H<sub>2</sub>S, as shown in Fig. 3. The selectivities to saturated hydrocarbons on the NiMo catalyst and to unsaturated hydrocarbons on the CoMo catalyst slightly decreased. At the same time, the selectivities to heptanol, heptanoic acid and heptyl heptanoate increased. The addition of H<sub>2</sub>S at all concentrations stabilised the selectivities as a function of time (Fig. 3b) and shifted the distribution of the main products. In the absence of the sulphiding agents, heptane on the NiMo catalyst and heptenes on the CoMo catalyst were formed as the main products from all the model compounds. The addition of H<sub>2</sub>S up to 1000 ppm shifted the main products of the esters to hexane on the NiMo catalyst and to hexenes on the CoMo catalyst. In the presence of 24,000 ppm H<sub>2</sub>S, however, hexenes became the main products on the NiMo catalyst. As a result, the molar ratios of saturated to unsaturated hydrocarbons dropped on the NiMo catalyst, but there was no substantial change on the CoMo catalyst (Table 4). When H<sub>2</sub>S was added, the main products of heptanol and heptanoic acid on the NiMo catalyst were heptenes and C<sub>6</sub> hydrocarbons, respectively. On the CoMo catalyst, the main products of the alcohol and the acid were heptenes.

Table 3  
Products detected in the liquid samples of the HDO experiments

	Hydrocarbon	Oxygen-containing compounds	Sulphur-containing compounds
Methyl heptanoate	C <sub>6</sub> <sup>a</sup> , C <sub>7</sub> <sup>b</sup>	Methanol, 1-heptanol, heptanal, <i>n</i> -heptanoic acid, heptyl heptanoate, dimethyl and diheptyl ether	1-Methanethiol, 1-hexanethiol, 1-heptanethiol, dimethyl and diheptyl sulphide, dissolved H <sub>2</sub> S
Ethyl heptanoate	C <sub>6</sub> <sup>a</sup> , C <sub>7</sub> <sup>b</sup>	Ethanol, 1-heptanol, heptanal, <i>n</i> -heptanoic acid, heptyl heptanoate, diethyl ether	1-Hexanethiol, 1-heptanethiol, diethyl and diheptyl sulphide, dissolved H <sub>2</sub> S
<i>n</i> -Heptanoic acid	C <sub>6</sub> <sup>a</sup> , C <sub>7</sub> <sup>b</sup>	1-Heptanol, heptyl heptanoate, heptanal, diheptyl ether	1-Hexanethiol, 1-heptanethiol
1-Heptanol	C <sub>7</sub> <sup>b</sup>	Diheptyl ether	1-Heptanethiol, diheptyl sulphide

<sup>a</sup> *n*-Hexane, 1-hexene, *cis/trans*-2-hexene and *cis/trans*-3-hexene.

<sup>b</sup> *n*-Heptane, 1-heptene, *cis/trans*-2-heptene and *cis/trans*-3-heptene.



NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	
■	Saturated hydrocarbons	◆	Saturated hydrocarbons
□	Unsaturated hydrocarbons	◇	Unsaturated hydrocarbons
▲	Oxygen-containing compounds	●	Oxygen-containing compounds

Fig. 3. Changes in selectivities as a function of time during the HDO of methyl heptanoate in the (a) absence of H<sub>2</sub>S and (b) presence of 1000 ppm H<sub>2</sub>S.

The changes in the selectivities with the addition of H<sub>2</sub>S were reflected in the yields of hydrocarbons, as seen in Fig. 4. With the addition of H<sub>2</sub>S, total yield of C<sub>7</sub> hydrocarbons decreased on the NiMo catalyst, but they were not affected noticeably on the CoMo catalyst (Fig. 5). In contrast to this, the yield of C<sub>6</sub> hydrocarbons increased on both catalysts (Fig. 5). Meanwhile, the total amount of oxygen-containing compounds dropped on both catalysts with increased H<sub>2</sub>S concentration in the feed. The yields of the products formed in the reactions of heptanoic acid changed with the addition of H<sub>2</sub>S in a similar way as in the reactions of the esters.

Table 4  
Effects of H<sub>2</sub>S and CS<sub>2</sub> on the molar ratios of saturated to unsaturated hydrocarbons formed in the reactions of methyl heptanoate and ethyl heptanoate on sulphided catalysts

	Methyl heptanoate					CS <sub>2</sub> (ppm)			Ethyl heptanoate		
	H <sub>2</sub> S (ppm)					CS <sub>2</sub> (ppm)			H <sub>2</sub> S (ppm)		
	0 <sup>a</sup>	140	500	1000 <sup>b</sup>	24,000	740	2200	3700	0	140	1000
NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (mol/mol)											
C <sub>7</sub> /C <sub>7</sub> <sup>=</sup>	7.6	4.8	4.5	1.8	0.5	0.6	0.4	0.4	7.6	6.8	2.0
C <sub>6</sub> /C <sub>6</sub> <sup>=</sup>	5.8	3.1	2.5	1.2	0.3	0.5	0.2	0.2	4.6	4.3	1.2
CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (mol/mol)											
C <sub>7</sub> /C <sub>7</sub> <sup>=</sup>	0.3	0.4	0.3	0.3	–	0.3	0.3	0.4	0.3	0.3	0.3
C <sub>6</sub> /C <sub>6</sub> <sup>=</sup>	0.2	0.2	0.2	0.2	–	0.3	0.3	0.2	0.2	0.2	0.2

<sup>a</sup> From Ref. [19].

<sup>b</sup> From Ref. [20].

### 3.2.2. Effect of CS<sub>2</sub> on product distribution

The addition of CS<sub>2</sub> decreased the molar ratio of saturated to unsaturated hydrocarbons on the NiMo catalyst, as seen in Table 4. The effect of CS<sub>2</sub> on the yields of hydrocarbons and heptanoic acid formed in the reactions of methyl heptanoate is presented in Fig. 6a. The yield of saturated hydrocarbons decreased with increased CS<sub>2</sub> concentration in the feed, while the yields of unsaturated hydrocarbons and of heptanoic acid increased. Total yield of hydrocarbons, however, dropped on the NiMo catalyst, and the acid became the main product in the presence of 2200 ppm CS<sub>2</sub> and above.

The addition of CS<sub>2</sub> decreased the yields of hydrocarbons on the CoMo catalyst (Fig. 6b). The decrease was more noticeable for the yield of C<sub>7</sub> hydrocarbons than the yield of C<sub>6</sub> hydrocarbons. The addition of CS<sub>2</sub> did not, however, noticeably alter the ratio of saturated to unsaturated hydrocarbons (Table 4).

## 4. Discussion

### 4.1. Effect of sulphiding agents on HDO

The enhanced total and HDO conversions and stabilised selectivities as a function of time in the presence of H<sub>2</sub>S clearly indicate a promoting effect of H<sub>2</sub>S on the reactions of the aliphatic oxygenates on the sulphided catalysts. The effect appears to be a function of H<sub>2</sub>S concentration up to 24,000 ppm. It should be noted that, although the ester conversion was highest in the presence of 24,000 ppm H<sub>2</sub>S, such a high concentration of H<sub>2</sub>S is not realistic in the industrial context. The role of hydrogenation and acid-catalysed (hydrolysis, esterification, dehydration) reactions was previously shown in the conversion of the aliphatic esters on the sulphided catalysts [19]. Fig. 7 presents the reaction scheme of the aliphatic methyl and ethyl esters on the basis of the results obtained in the absence of a sulphiding agent in the feed. In the literature, the presence of sulphiding agents has been reported to increase the acidity of sulphided catalysts [21–23]. Thus, the promotion by H<sub>2</sub>S seems to be a consequence of the increased catalyst acidity.

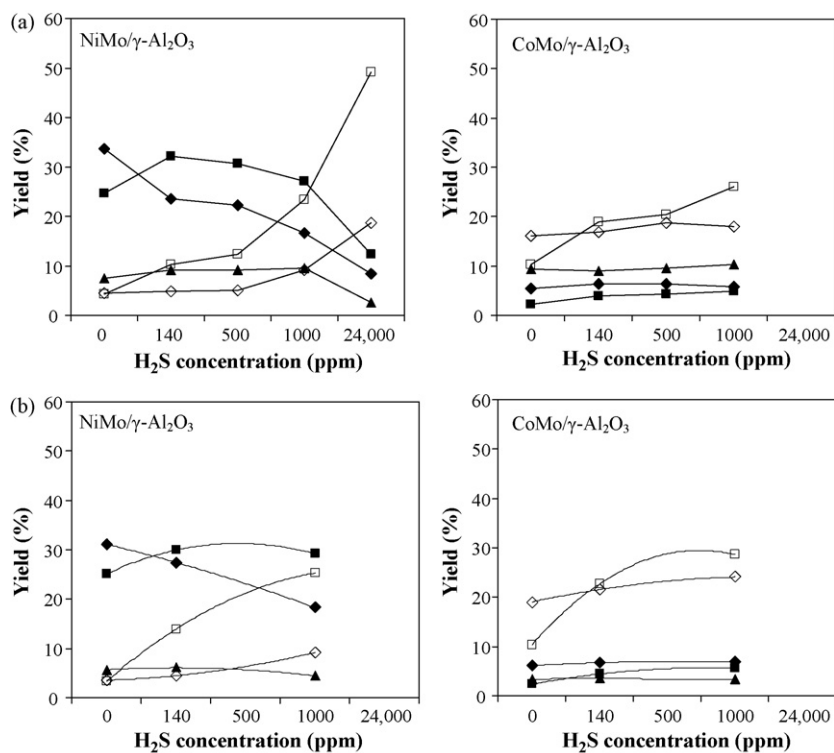


Fig. 4. Effect of H<sub>2</sub>S on the yields of heptane (◆), hexane (■), heptenes (◇), hexenes (□) and heptanoic acid (▲) formed in the reactions of (a) methyl heptanoate and (b) ethyl heptanoate on the sulphided catalysts.

H<sub>2</sub>S shifted the main products of the esters and the acid from C<sub>7</sub> to C<sub>6</sub> hydrocarbons, and the yields of C<sub>6</sub> hydrocarbons increased on both catalysts (Fig. 5). These results suggest an enhancement particularly in the routes to C<sub>6</sub> hydrocarbons. Although the yields of C<sub>7</sub> hydrocarbons were practically unaffected in the reactions of the esters and the acid when H<sub>2</sub>S was added (Fig. 5), the improved conversions in the experiments with heptanol clearly indicate that the sulphiding agent had a promoting effect on the dehydration reaction. It is probable, therefore, that the routes to heptanol (Fig. 7) were suppressed by the sulphiding agent, and the formation of C<sub>7</sub> hydrocarbons was limited by the concentration effect of heptanol. The changes in the product distributions with the addition of H<sub>2</sub>S will, according to Fig. 7, lead to a reduction in the total consumption of hydrogen, which may be industrially desirable. At the same time, the formation of carbon oxides increases, and the carbon efficiency decreases as a result.

Clearly, the effects of H<sub>2</sub>S on the HDO of the aliphatic esters differ from those on the HDO of phenols [10–12] and the HDS of dibenzothiophenes [13–17] on similar sulphided catalysts. Apparently, the active sites and/or reaction mechanisms associated with the reactions of the aliphatic oxygenates are different from those associated with the reactions of dibenzothiophenes and phenols. On the other hand, the HDN studies with aliphatic and cyclic alkylamines and indole on sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts showed the addition of sulphiding agents to have an enhancing effect, due to the increased catalyst acidity [24–27]. In this respect, the promotion of the HDO of the aliphatic oxygenates can be

compared with the promotion of the HDN of the nitrogen-containing compounds.

CS<sub>2</sub> should decompose under the reaction conditions and produce H<sub>2</sub>S and CH<sub>4</sub>. That being true, CS<sub>2</sub> and H<sub>2</sub>S could be expected to have similar effects on the catalyst activities. In contrast to the addition of H<sub>2</sub>S, however, the addition of CS<sub>2</sub> up to 3700 ppm in the feed had no clear effect on the total ester conversions (Fig. 2), but the formation of hydrocarbons, i.e. the HDO conversions, was diminished. Evidently, CS<sub>2</sub> had an inhibiting effect on the HDO, attributable perhaps to the notable increase in the carbon contents of the catalysts when CS<sub>2</sub> was added, as compared with the only weak increase when H<sub>2</sub>S was added (Table 1). It should be noted that the decomposition of CS<sub>2</sub> under the reaction conditions is in principle expected to consume hydrogen, and hence reduce the amount of hydrogen available for the reactions. The amount of hydrogen fed to the reactor in the present study was, nevertheless, high enough for the reactions. As a conclusion, for the HDO of the aliphatic oxygenates under the conditions of this study, the use of H<sub>2</sub>S as the sulphiding agent seems to be more beneficial than the use of CS<sub>2</sub>.

#### 4.2. Effect of sulphiding agents on hydrogenation

The effect of H<sub>2</sub>S on the hydrogenation reactions can be evaluated through study of the molar ratios of saturated to unsaturated hydrocarbons. Decreasing ratios on the NiMo catalyst with increasing H<sub>2</sub>S and CS<sub>2</sub> concentrations (Table 4) reveal an inhibition effect. In contrast to this, the presence of sulphiding agent did not change the molar ratios on the CoMo

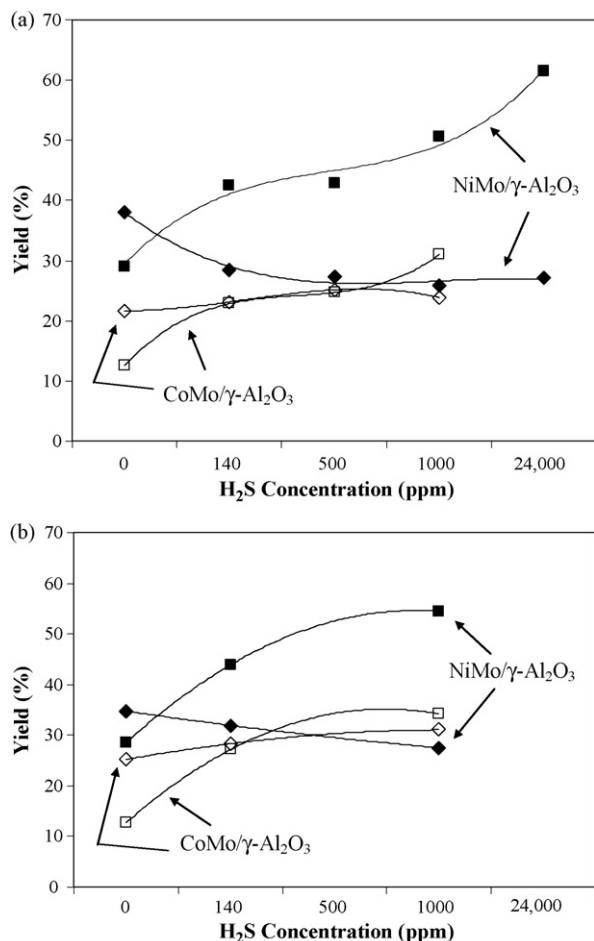


Fig. 5. Effect of H<sub>2</sub>S on the yields of C<sub>7</sub> (◆, ◇) and C<sub>6</sub> (■, □) hydrocarbons formed in the reactions of (a) methyl heptanoate and (b) ethyl heptanoate on the sulphided catalysts.

catalyst, indicating no significant effect on the hydrogenation reactions. These observations are in good agreement with the effect of H<sub>2</sub>S reported in the literature [14,25,27]. H<sub>2</sub>S was generally found to inhibit the hydrogenation reactions on sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts, and it affected them insignificantly on sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. Any reduction in the hydrogenation activity likely influences the other steps in which hydrogen is involved, e.g. the formation of heptanol (Fig. 7). Consequently, the rate of heptanol formation can decrease in the presence of H<sub>2</sub>S, resulting in the concentration effect mentioned above.

#### 4.3. Catalytic sites

Coordinatively unsaturated sites (CUS) associated with the MoS<sub>2</sub> phase, i.e. sulphur anion vacancies, on the sulphided catalysts show Lewis acid character, and they are generally considered to catalyse the reactions in hydroprocessing [4,8]. The surface of the sulphided catalyst also includes groups such as S<sup>2-</sup>, SH<sup>-</sup> and H<sup>+</sup> [21,22]. The SH<sup>-</sup> and H<sup>+</sup> groups exhibit Brønsted acid character and are formed by dissociative adsorption of H<sub>2</sub>S on the vacancies [21–23]. The dissociation also turns the S<sup>2-</sup> groups into SH<sup>-</sup> groups. Thus, the Brønsted

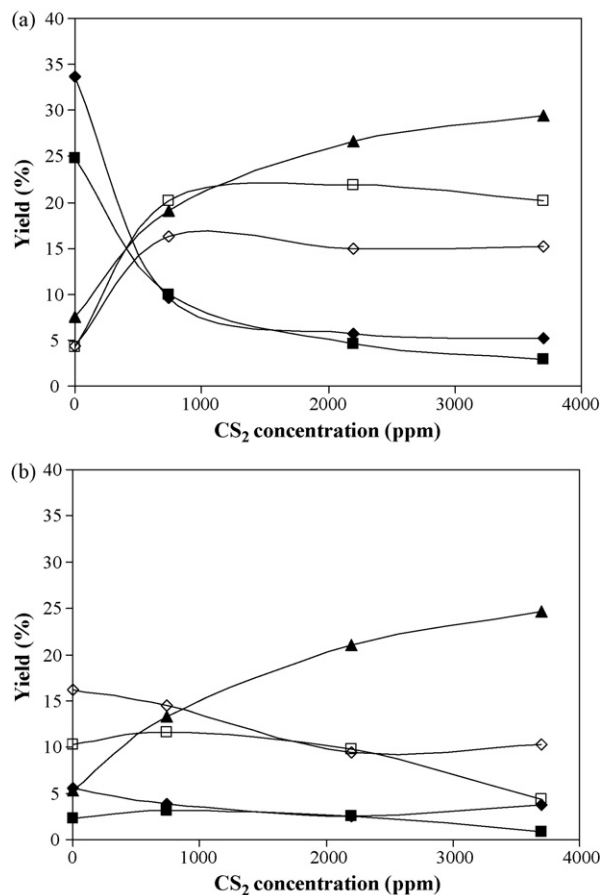


Fig. 6. Effect of CS<sub>2</sub> on the yields of heptane (◆), hexane (■), heptenes (◇), hexenes (□) and heptanoic acid (▲) formed in the reactions of methyl heptanoate on the sulphided (a) NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and (b) CoMo/γ-Al<sub>2</sub>O<sub>3</sub> catalysts.

acidity of the catalyst increases, while the Lewis acidity decreases when H<sub>2</sub>S was added [23]. The SH<sup>-</sup> groups might be involved both in supplying hydrogen for hydroprocessing reactions and providing Brønsted acidity for acid-catalysed reactions [21].

On this view, the promotion by H<sub>2</sub>S may be explained as follows. As we proposed in our recent study [19], unsaturated hydrocarbons may be formed by E<sub>2</sub> elimination reaction and the sulphur-containing compounds and ethers by S<sub>N</sub>2 nucleophilic substitution reaction. The SH<sup>-</sup> groups, i.e. Brønsted acidity, play a role in these reactions. Thus, the

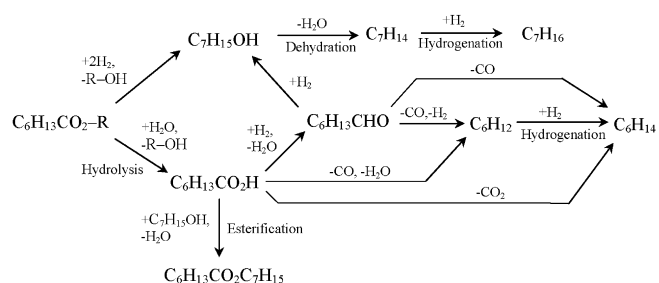


Fig. 7. Reactions of methyl heptanoate (R = CH<sub>3</sub>) and ethyl heptanoate (R = C<sub>2</sub>H<sub>5</sub>) on the sulphided catalysts.



increasing Brønsted acidity in the presence of H<sub>2</sub>S probably promoted the acid-catalysed E<sub>2</sub> elimination and S<sub>N</sub>2 nucleophilic substitution reactions. Sulphur-containing compounds were detected only in trace amounts possibly because of their fast decomposition to a hydrocarbon and H<sub>2</sub>S under the reaction conditions. The formation of C<sub>6</sub> hydrocarbons may, however, be explained by the addition of a hydrogen atom to the α-carbon atom with respect to the oxygen atom of the adsorbed species followed by the elimination of the whole carboxylic group. According to this mechanism, since more SH<sup>-</sup> groups will be present on the surface when the sulphiding agent is added, enhancement of the hydrogen transfer and/or the acidity needed for the elimination of the carboxylic group would be expected.

Although the role of sulphur anion vacancies in the rupture of carbon-heteroatom bond is generally acknowledged, there appears to be substantial disagreement regarding the catalytic sites involved in the hydrogenation reactions. Many authors have proposed that the hydrogenation reactions, too, occur on the sulphur anion vacancies (CUS), and the degree of the saturation of CUS for the hydrogenation reactions is different from those for the rupture of carbon-heteroatom bonds, making the sites for the hydrogenation reactions less electrophilic than those associated with the carbon-heteroatom bond scission [10,27–29]. According to this model, the inhibition of the hydrogenation reactions on the NiMo catalyst may be attributed to the saturation of the less electrophilic hydrogenation sites. However, this does not explain why the hydrogenation reactions were scarcely affected on the CoMo catalyst. An explanation of this may be provided by recent scanning tunnelling microscopy investigations and density functional theory calculations, which have revealed that metallic-like so-called brim sites, not sulphur anion vacancies (CUS), on sulphided catalysts are involved in the hydrogenation reactions [30,31]. The brim sites have been shown to be fully coordinated by sulphur, and therefore they do not interact strongly with H<sub>2</sub>S. The brim sites may, thus, be involved in the hydrogenation reactions on the CoMo catalyst.

#### 4.4. Effect of the sulphiding agents on catalyst stability

Comparison of the total ester conversions on the NiMo and CoMo catalysts (Fig. 1) revealed a higher activity for the NiMo catalyst in both absence and presence of the sulphiding agents. As the hydrogenation and acid-catalysed reactions play a role in the HDO of the aliphatic oxygenates, the better performance of the NiMo catalyst can be explained in terms of its higher acidity [32] and hydrogenation capacity.

Although H<sub>2</sub>S stabilised the selectivities and improved the conversions, the total conversions showed a similar decreasing trend as a function of time as they did in the absence of H<sub>2</sub>S. Evidently, the addition of H<sub>2</sub>S does not protect the catalysts from deactivation. The situation did not change when CS<sub>2</sub> was added to the feed. Coke formation and desulphurisation are known to cause the deactivation of sulphided catalysts [4,8]. Accordingly, the changes in the carbon and sulphur contents of the catalysts (Table 1) might explain the deactivation. It is worth noting that the amounts of sulphiding agents added to the

feed were sufficient to maintain the sulphidation level of the NiMo catalyst (Table 1). The formation of sulphur-containing compounds was likely associated with the catalyst desulphurisation.

## 5. Conclusions

H<sub>2</sub>S had a promoting effect on the overall activity of sulphided NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and CoMo/γ-Al<sub>2</sub>O<sub>3</sub> catalysts for the conversion of the aliphatic esters, but it did not prevent the catalyst deactivation. Furthermore, the promoting effect of H<sub>2</sub>S increased with its amount in the feed. In contrast, the addition of CS<sub>2</sub>, which produces H<sub>2</sub>S under the reaction conditions, did not affect the total conversion noticeably and suppressed the HDO conversion on the catalysts.

The addition of H<sub>2</sub>S favoured the acid-catalysed reactions, evidently by increasing catalyst acidity. The addition of CS<sub>2</sub>, however, suppressed these reactions, possibly due to the hindrance of the acidic sites by coke. Both H<sub>2</sub>S and CS<sub>2</sub> inhibited the hydrogenation reactions on the NiMo catalyst but not on the CoMo catalyst. As a result, the addition of H<sub>2</sub>S shifted the main products from C<sub>7</sub> to C<sub>6</sub> hydrocarbons, and it led to an increase in the formation of carbon oxides (CO and CO<sub>2</sub>). This indicates a decrease in carbon efficiency. On the positive side, the hydrogen consumption decreased.

In conclusion, the use of H<sub>2</sub>S as the sulphiding agent in the HDO of aliphatic oxygenates is more beneficial than the use of CS<sub>2</sub>. However, the concentration of H<sub>2</sub>S added to the HDO feed should be carefully controlled since the amount of H<sub>2</sub>S influences the overall HDO, the consumption of hydrogen, the formation of environmentally unfavourable gases, the carbon efficiency and, last but not least, the degree of hydrocarbon saturation.

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