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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 H₂S and CS₂ on the HDO of aliphatic esters on sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ 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 C₇ and C₆ hydrocarbons in reactions where oxygen- and sulphur-containing compounds were formed as intermediates. Unlike CS₂, H₂S had a promoting effect on the HDO of the aliphatic oxygenates. The addition of H₂S stabilised the selectivities as a function of time, and shifted the main products from C₇ to C₆ hydrocarbons, but did not prevent catalyst deactivation. The promoting effect of H₂S was attributed to the increased catalyst acidity, which enhanced the acid-catalysed reactions (hydrolysis, esterification, dehydration, E₂ elimination and S_N2 nucleophilic substitution). Both H₂S and CS₂ suppressed the hydrogenation reactions on the NiMo catalyst but did not affect them significantly on the CoMo catalyst. H₂S induced less hydrogen consumption and coke formation than CS₂, but the carbon efficiency suffered in the presence of H₂S. Thus, the use of H₂S as sulphiding agent in the HDO of the aliphatic oxygenates was concluded to be more beneficial than the use of CS₂. © 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/Al₂O₃ and CoMo/Al₂O₃ catalysts. Moreover, the addition of H₂S reportedly suppresses the activity of sulphided NiMo/Al₂O₃ catalyst for the conversion of ketonic groups, but

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has no effect on the activity of sulphided CoMo/Al₂O₃ catalyst [18]. On both catalysts, H₂S 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 H₂S 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/Al₂O₃ and CoMo/Al₂O₃ catalysts with H₂S 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 CS₂. Potential catalytic sites are discussed on the basis of the obtained data.

2. Experimental

2.1. Catalytic runs

Commercial NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ 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% H₂S/H₂ mixture (AGA, 99.999%) was blended with hydrogen (AGA, 99.999%) feed at various flow rates to obtain 140, 500 or 1000 ppm H₂S in molar basis in the reactor. An additional run with the NiMo catalyst was carried out by adding a very high H₂S 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 CS₂ was studied, experiments were performed by adding CS₂ (Merck, >99.7%) to a liquid feed that contained 3 wt% methyl heptanoate. The concentration of CS₂ 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 H₂S on the reactions, additional experiments were performed in the presence of H₂S 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 H₂S [19]. Experiments with heptanoic acid were carried out with 0.5 g catalyst loading and 3 wt% acid in *m*-xylene. The concentration of H₂S 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 H₂S 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

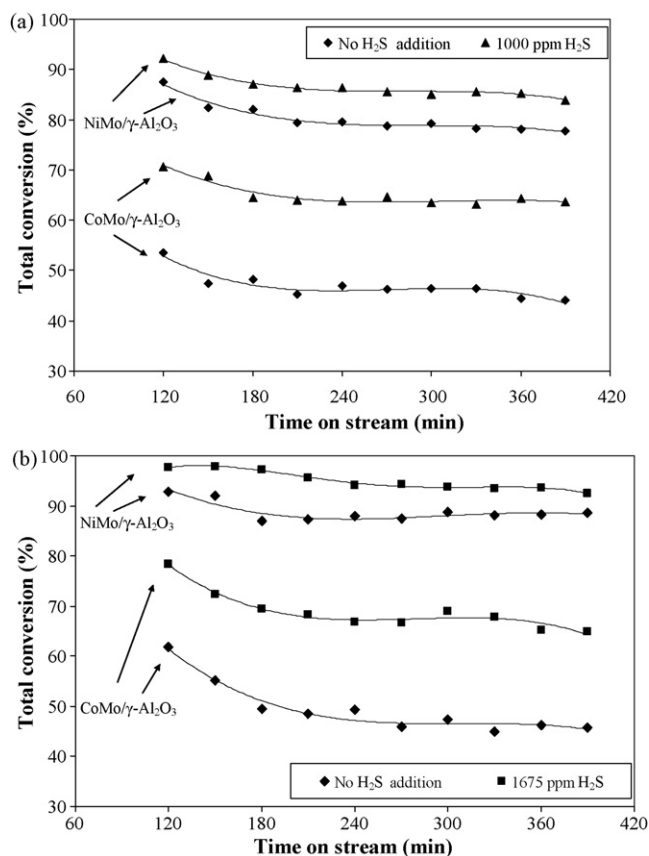


Fig. 1. Effect of H₂S on the total conversion of (a) methyl heptanoate and (b) heptanoic acid on the sulphided catalysts as a function of time.

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 ± 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 H₂S on the total and HDO conversions of 1-heptanol and *n*-heptanoic acid on sulphided catalysts

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

^a Reaction products detected in liquid samples included C₇ hydrocarbons, diheptyl ether, 1-heptanethiol and diheptyl sulphide.

^b Reaction products detected in liquid samples included C₆ and C₇ hydrocarbons, 1-heptanol, heptyl heptanoate, heptanal, diheptyl ether, 1-hexanethiol and 1-heptanethiol.

^c 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 H₂S in the feed. However, comparison of the carbon contents in the presence of H₂S and CS₂ revealed greater carbon deposition in the presence of CS₂ (Table 1).

3.1.2. Effects of H₂S and CS₂ on catalyst activities

On both catalysts, the total ester conversions increased with the concentration of H₂S in the feed, as seen in Fig. 2. The HDO conversions increased as well. With the addition of 1000 ppm H₂S, 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 ₂ S (ppm)					CS ₂ (ppm)			H ₂ S (ppm)		
	0 ^a	140	500	1000 ^b	24,000	740	2200	3700	0	140	1000
NiMo/γ-Al ₂ O ₃											
Sulphur (wt%) ^c	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 ₂ O ₃											
Sulphur (wt%) ^c	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

^a From Ref. [19].

^b From Ref. [20].

^c Sulphur content of the catalyst on carbon-free basis (7.0 ± 0.3 wt% before the reactions).

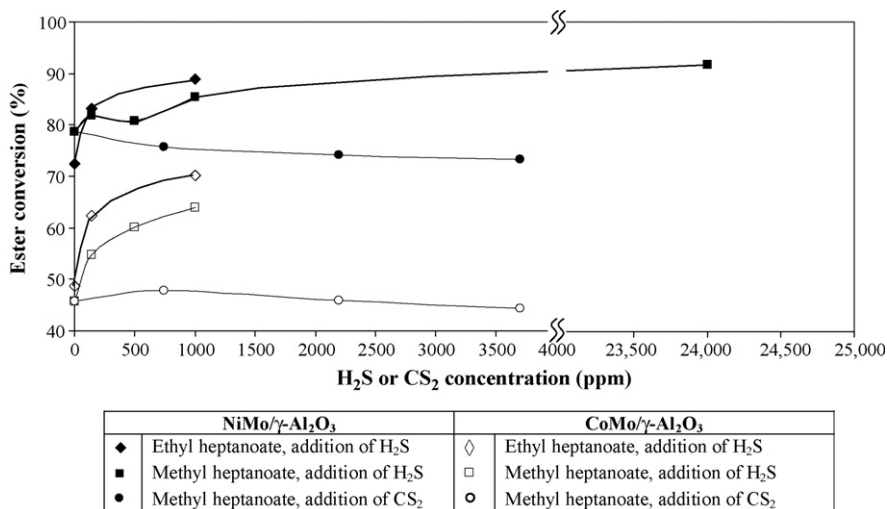


Fig. 2. Effects of addition of H₂S and CS₂ on the total conversions of methyl and ethyl heptanoate on the sulphided catalysts.

Likewise, the addition of H₂S improved the total and HDO conversions of heptanol and heptanoic acid, as shown in Table 2.

The addition of CS₂, 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 CS₂, 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 (CO₂ 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 H₂S on product distribution

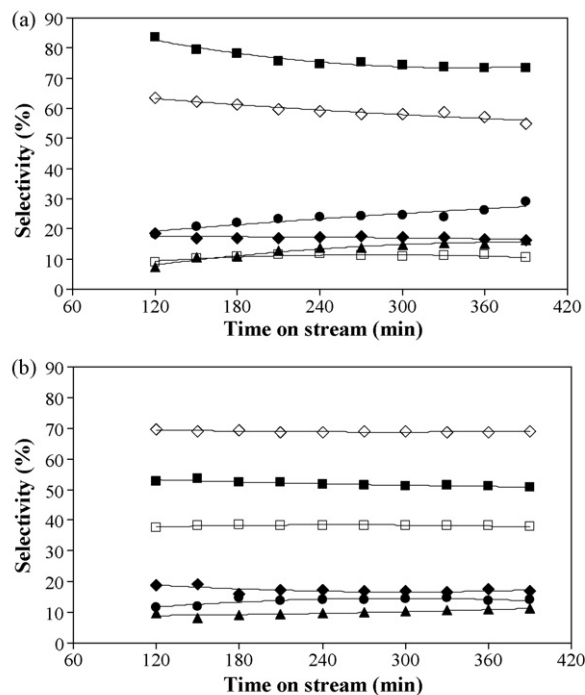
In the absence of H₂S, on both catalysts, the selectivities to hydrocarbons changed as a function of time. For instance, product selectivities changed as a function of time during the HDO of methyl heptanoate in the absence and presence of 1000 ppm H₂S, as shown in Fig. 3. The selectivities to saturated 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 H₂S 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 H₂S 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 H₂S, 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 H₂S was added, the main products of heptanol and heptanoic acid on the NiMo catalyst were heptenes and C₆ 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 ₆ ^a , C ₇ ^b	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 ₂ S
Ethyl heptanoate	C ₆ ^a , C ₇ ^b	Ethanol, 1-heptanol, heptanal, <i>n</i> -heptanoic acid, heptyl heptanoate, diethyl ether	1-Hexanethiol, 1-heptanethiol, diethyl and diheptyl sulphide, dissolved H ₂ S
<i>n</i> -Heptanoic acid	C ₆ ^a , C ₇ ^b	1-Heptanol, heptyl heptanoate, heptanal, diheptyl ether	1-Hexanethiol, 1-heptanethiol
1-Heptanol	C ₇ ^b	Diheptyl ether	1-Heptanethiol, diheptyl sulphide

^a *n*-Hexane, 1-hexene, *cis/trans*-2-hexene and *cis/trans*-3-hexene.

^b *n*-Heptane, 1-heptene, *cis/trans*-2-heptene and *cis/trans*-3-heptene.



NiMo/γ-Al ₂ O ₃		CoMo/γ-Al ₂ O ₃	
■	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 H₂S and (b) presence of 1000 ppm H₂S.

The changes in the selectivities with the addition of H₂S were reflected in the yields of hydrocarbons, as seen in Fig. 4. With the addition of H₂S, total yield of C₇ 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 C₆ hydrocarbons increased on both catalysts (Fig. 5). Meanwhile, the total amount of oxygen-containing compounds dropped on both catalysts with increased H₂S concentration in the feed. The yields of the products formed in the reactions of heptanoic acid changed with the addition of H₂S in a similar way as in the reactions of the esters.

Table 4
Effects of H₂S and CS₂ 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 ₂ (ppm)			Ethyl heptanoate		
	H ₂ S (ppm)								H ₂ S (ppm)		
	0 ^a	140	500	1000 ^b	24,000	740	2200	3700	0	140	1000
NiMo/γ-Al ₂ O ₃ (mol/mol)											
C ₇ /C ₇ ⁼	7.6	4.8	4.5	1.8	0.5	0.6	0.4	0.4	7.6	6.8	2.0
C ₆ /C ₆ ⁼	5.8	3.1	2.5	1.2	0.3	0.5	0.2	0.2	4.6	4.3	1.2
CoMo/γ-Al ₂ O ₃ (mol/mol)											
C ₇ /C ₇ ⁼	0.3	0.4	0.3	0.3	–	0.3	0.3	0.4	0.3	0.3	0.3
C ₆ /C ₆ ⁼	0.2	0.2	0.2	0.2	–	0.3	0.3	0.2	0.2	0.2	0.2

^a From Ref. [19].

^b From Ref. [20].

3.2.2. Effect of CS₂ on product distribution

The addition of CS₂ decreased the molar ratio of saturated to unsaturated hydrocarbons on the NiMo catalyst, as seen in Table 4. The effect of CS₂ 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 CS₂ 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 CS₂ and above.

The addition of CS₂ decreased the yields of hydrocarbons on the CoMo catalyst (Fig. 6b). The decrease was more noticeable for the yield of C₇ hydrocarbons than the yield of C₆ hydrocarbons. The addition of CS₂ 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 H₂S clearly indicate a promoting effect of H₂S on the reactions of the aliphatic oxygenates on the sulphided catalysts. The effect appears to be a function of H₂S concentration up to 24,000 ppm. It should be noted that, although the ester conversion was highest in the presence of 24,000 ppm H₂S, such a high concentration of H₂S 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 H₂S seems to be a consequence of the increased catalyst acidity.

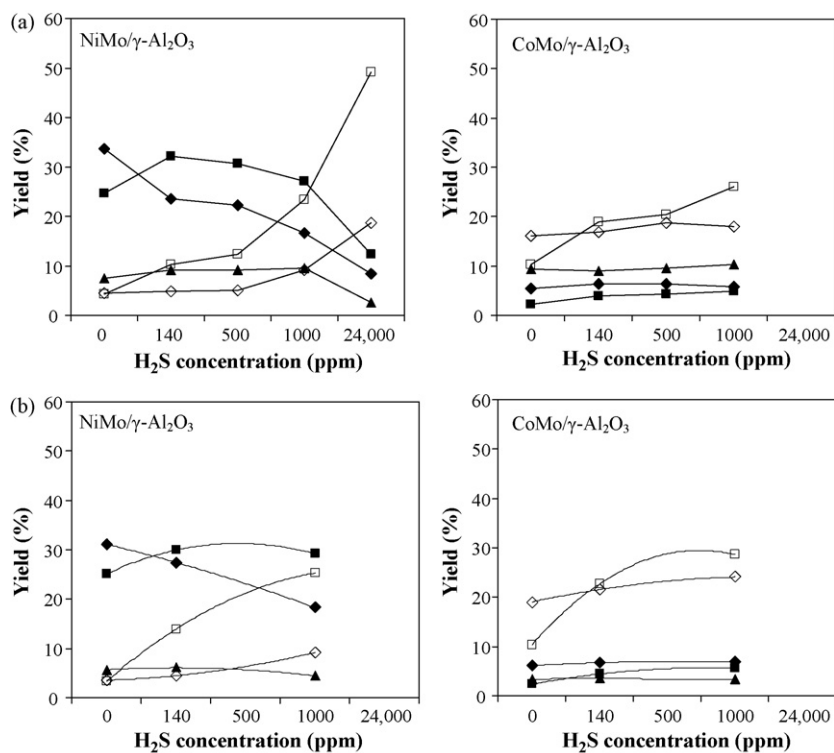


Fig. 4. Effect of H₂S on the yields of heptane (◆), hexane (■), heptenes (◇), hexenes (□) and heptanoic acid (▲) formed in the reactions of (a) methyl heptanoate and (b) ethyl heptanoate on the sulphided catalysts.

H₂S shifted the main products of the esters and the acid from C₇ to C₆ hydrocarbons, and the yields of C₆ hydrocarbons increased on both catalysts (Fig. 5). These results suggest an enhancement particularly in the routes to C₆ hydrocarbons. Although the yields of C₇ hydrocarbons were practically unaffected in the reactions of the esters and the acid when H₂S 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 C₇ hydrocarbons was limited by the concentration effect of heptanol. The changes in the product distributions with the addition of H₂S 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 H₂S 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/Al₂O₃ and CoMo/Al₂O₃ 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.

CS₂ should decompose under the reaction conditions and produce H₂S and CH₄. That being true, CS₂ and H₂S could be expected to have similar effects on the catalyst activities. In contrast to the addition of H₂S, however, the addition of CS₂ 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, CS₂ had an inhibiting effect on the HDO, attributable perhaps to the notable increase in the carbon contents of the catalysts when CS₂ was added, as compared with the only weak increase when H₂S was added (Table 1). It should be noted that the decomposition of CS₂ 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 H₂S as the sulphiding agent seems to be more beneficial than the use of CS₂.

4.2. Effect of sulphiding agents on hydrogenation

The effect of H₂S 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 H₂S and CS₂ 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

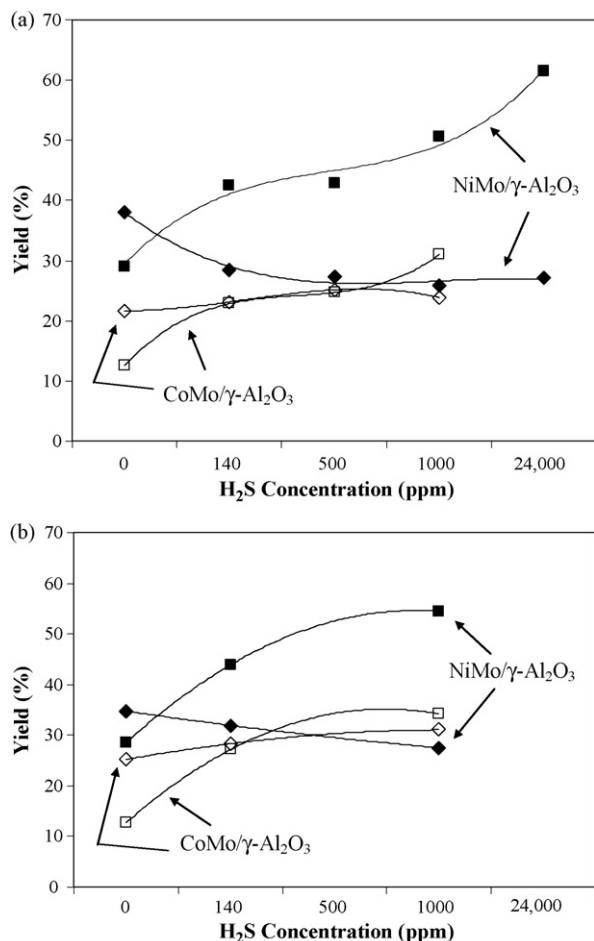


Fig. 5. Effect of H₂S on the yields of C₇ (◆, ◇) and C₆ (■, □) hydrocarbons formed in the reactions of (a) methyl heptanoate and (b) ethyl heptanoate on the sulphided catalysts.

catalyst, indicating no significant effect on the hydrogenation reactions. These observations are in good agreement with the effect of H₂S reported in the literature [14,25,27]. H₂S was generally found to inhibit the hydrogenation reactions on sulphided NiMo/Al₂O₃ catalysts, and it affected them insignificantly on sulphided CoMo/Al₂O₃ 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 H₂S, resulting in the concentration effect mentioned above.

4.3. Catalytic sites

Coordinatively unsaturated sites (CUS) associated with the MoS₂ 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 S²⁻, SH⁻ and H⁺ [21,22]. The SH⁻ and H⁺ groups exhibit Brønsted acid character and are formed by dissociative adsorption of H₂S on the vacancies [21–23]. The dissociation also turns the S²⁻ groups into SH⁻ groups. Thus, the Brønsted

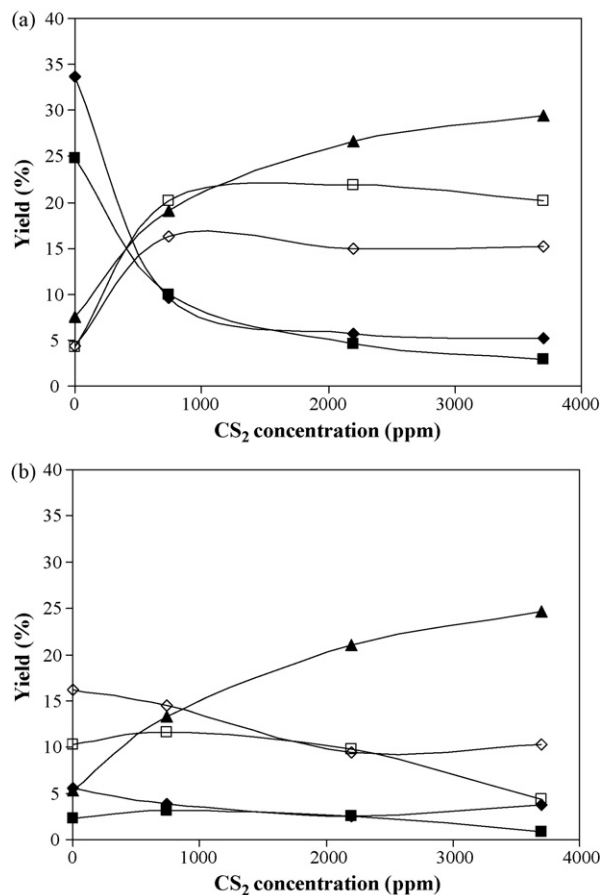


Fig. 6. Effect of CS₂ on the yields of heptane (◆), hexane (■), heptenes (◇), hexenes (□) and heptanoic acid (▲) formed in the reactions of methyl heptanoate on the sulphided (a) NiMo/γ-Al₂O₃ and (b) CoMo/γ-Al₂O₃ catalysts.

acidity of the catalyst increases, while the Lewis acidity decreases when H₂S was added [23]. The SH⁻ 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 H₂S may be explained as follows. As we proposed in our recent study [19], unsaturated hydrocarbons may be formed by E₂ elimination reaction and the sulphur-containing compounds and ethers by S_N2 nucleophilic substitution reaction. The SH⁻ groups, i.e. Brønsted acidity, play a role in these reactions. Thus, the

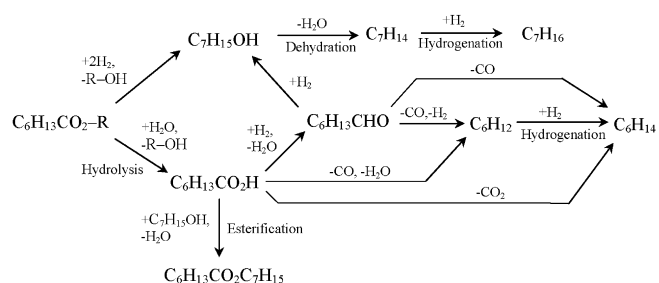


Fig. 7. Reactions of methyl heptanoate (R = CH₃) and ethyl heptanoate (R = C₂H₅) on the sulphided catalysts.

increasing Brønsted acidity in the presence of H₂S probably promoted the acid-catalysed E₂ elimination and S_N2 nucleophilic substitution reactions. Sulphur-containing compounds were detected only in trace amounts possibly because of their fast decomposition to a hydrocarbon and H₂S under the reaction conditions. The formation of C₆ 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⁻ 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 H₂S. 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 H₂S 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 H₂S. Evidently, the addition of H₂S does not protect the catalysts from deactivation. The situation did not change when CS₂ 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

H₂S had a promoting effect on the overall activity of sulphided NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃ catalysts for the conversion of the aliphatic esters, but it did not prevent the catalyst deactivation. Furthermore, the promoting effect of H₂S increased with its amount in the feed. In contrast, the addition of CS₂, which produces H₂S under the reaction conditions, did not affect the total conversion noticeably and suppressed the HDO conversion on the catalysts.

The addition of H₂S favoured the acid-catalysed reactions, evidently by increasing catalyst acidity. The addition of CS₂, however, suppressed these reactions, possibly due to the hindrance of the acidic sites by coke. Both H₂S and CS₂ inhibited the hydrogenation reactions on the NiMo catalyst but not on the CoMo catalyst. As a result, the addition of H₂S shifted the main products from C₇ to C₆ hydrocarbons, and it led to an increase in the formation of carbon oxides (CO and CO₂). This indicates a decrease in carbon efficiency. On the positive side, the hydrogen consumption decreased.

In conclusion, the use of H₂S as the sulphiding agent in the HDO of aliphatic oxygenates is more beneficial than the use of CS₂. However, the concentration of H₂S added to the HDO feed should be carefully controlled since the amount of H₂S 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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