Hydrodeoxygenation of methyl esters on sulphided NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃ catalysts

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Abstract

Wood-derived bio-oil contains high amounts of compounds with different oxygen-containing functional groups that must be removed to improve the fuel characteristics. Elimination of oxygen from carboxylic groups was studied with model compounds, methyl heptanoate and methyl hexanoate, on sulphided NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃ catalysts in a flow reactor. Catalyst performances and reaction schemes were addressed. Aliphatic methyl esters produced hydrocarbons via three main paths: The first path gave alcohols followed by dehydration to hydrocarbons. Deesterification yielded an alcohol and a carboxylic acid in the second path. Carboxylic acid was further converted to hydrocarbons either directly or with an alcohol intermediate. Decarboxylation of the esters led to hydrocarbons in the third path. No oxygen-containing compounds were detected at complete conversions. However, the product distributions changed with time, even at complete conversions, indicating that both catalysts deactivated under the studied conditions.
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1. Introduction

The European Union has set an objective of 20% substitution of conventional fuels with alternative fuels in the road transport sector by the year 2020 [1]. Therefore, efforts in research and development for biomass utilisation have increased. One major effort is directed towards improving the properties of biomass-derived liquid fuels.

The oxygen content of wood-derived bio-oil can be as high as 50 wt% mainly resulting from phenols and furans [2]. However, esters, carboxylic acids, aliphatic and aromatic alcohols, ethers, ketones and aldehydes have also been detected in significant amounts in these oils [3]. All these oxygenates are responsible for some deleterious properties of bio-oil: high viscosity, non-volatility, poor heating value, corrosiveness, immiscibility with fossil fuels, thermal instability and tendency to polymerise during storage and transportation [2,4,5]. Therefore, upgrading of

bio-oils by reducing their oxygen content is required. Hydrodeoxygenation (HDO), which occurs during hydroprocessing, refers to the process to obtain oxygen-free molecules [2]. Sulphided hydrotreating catalysts such as CoMo/Al₂O₃ and NiMo/Al₂O₃ are commonly utilised in HDO [2,6]. Stability and selectivity of the catalysts are crucial, as interaction of oxygen-containing compounds with the catalysts can modify the sulphide structure of the catalysts [2].

HDO of oxygen-containing compounds other than phenols and furans has received little attention due to their smaller amounts in bio-oils [2–5,7]. It is, however, important to know the reaction paths of different oxygen-containing molecules as well as their effect on the HDO catalysts. So far, we have studied the reactivity of phenol and its derivates [4,8–10]. In the present study, we focused on aliphatic methyl esters to investigate the HDO of oxygen-containing compounds with carboxylic functional groups. Activities of commercial hydrotreating catalysts CoMo/γ-Al₂O₃ and NiMo/γ-Al₂O₃ were tested with the model compounds methyl heptanoate and methyl hexanoate. HDO reaction schemes of the esters were presented.

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2. Experimental

Experiments were carried out in a tubular continuous flow reactor made of stainless steel (i.d. = 10 mm, $l = 380$ mm) under isothermal conditions at 250 °C. The reactor was heated with an electrical furnace, and the catalyst bed temperature was measured with a thermocouple in the reactor. Liquid samples were withdrawn via a cooled sampling vessel.

Reactions of methyl heptanoate (Fluka Chemika, >99%) and methyl hexanoate (Fluka Chemika, >99%) were studied on commercial NiMo/γ-Al$_2$O$_3$ and CoMo/γ-Al$_2$O$_3$ hydro-treatment catalysts in either oxide or sulphided form. Additionally, heptanoic acid (Aldrich, 99%) was used to study the reactions of a potential intermediate. Thermo-dynamic calculations predicted that under the studied conditions all the components are in a gas phase. A batch of 0.5 g of NiMo/γ-Al$_2$O$_3$ or CoMo/γ-Al$_2$O$_3$ (0.59–0.75 mm) catalyst was packed into the reactor between two layers of silicon carbide (1–3 mm). The catalyst was calcined under nitrogen (AGA 99.999%) with a flow of 2.5 l/h (NTP) for 2 h at 400 °C under atmospheric pressure. The sulphided catalysts were prepared in situ with 5 vol.% H$_2$S/H$_2$ mixture (AGA, 99.999%) at 400 °C under atmospheric pressure. Presulphidation was continued for 4 h with the gas flow rate of 2.5 l/h (NTP).

Following the presulphidation, the temperature was decreased to the reaction temperature of 250, 275 or 300 °C and the system pressure was increased to 1.5 MPa with hydrogen (AGA, 99.999%). The liquid feed containing one of the model compounds (3 wt%) in m-xylene (Merck, >99%) was fed to the reactor at a rate of 10 g/h. The hydrogen flow rate was kept at 2.0 l/h (NTP) during the experiment. After 2 h of stabilisation, the first liquid sample

was withdrawn. The liquid samples were collected at intervals of 30 min and analysed with a gas chromatograph (HP 6890 series) equipped with an HP-1 column and a flame ionisation detector. Cumene (Fluka Chemika, >98%) was used as the internal standard for the analyses. The gas phase of a few experiments was analysed qualitatively with a gas chromatograph (HP 5890A, thermal conductivity detector, packed column of activated carbon with 2% squalane). Carbon and sulphur contents of the catalysts were measured using a LECO elemental analysis instrument (SC-444 series). The accuracy of the sulphur analyses was ±0.2%.

Thermal reactions and the activity of the support were tested in separate runs at 300 °C using the reactor filled with silicon carbide and γ-Al$_2$O$_3$ (0.42–0.59 mm), respectively.

3. Results and discussion

3.1. Reaction products

Both esters yielded a number of alkenes, alkanes, alcohols and carboxylic acids. The identified products of methyl heptanoate in the liquid phase included n-heptane, n-hexane, 1-heptene, cis- and trans-2-heptene, 3-heptene, 1-hexene, cis- and trans-2-hexene, 3-hexene, methanol, 1-heptanol and heptanoic acid. Some heptyl heptanoate was also detected at 250 °C. Likewise, methyl hexanoate produced n-hexane, n-pentane, 1-hexene, cis- and trans-2-hexene, trans-3-hexene, 1-pentene, cis- and trans-2-pentene, methanol, 1-hexanol and hexanoic acid. In addition, carbon dioxide and methane were detected with some unidentified peaks in the gas phase from both esters. A summary of the results is presented in Table 1.

Table 1
Hydrotreatment of methyl heptanoate and methyl hexanoate

	NiMo/γ-Al$_2$O$_3$				CoMo/γ-Al$_2$O$_3$				γ-Al$_2$O$_3$
	Oxide[a]	Sulphided[a]			Oxide[a]	Sulphided[a]			
	300[b]	250[b]	275[b]	300[b]	300[b]	250[b]	275[b]	300[b]	300[b]
Methyl heptanoate									
Average conversion (%)	43.2	80.0	100	100	13.0	46.6	78.4	100	12.6
Hydrocarbon yield (%)[c]	10.5	60.9	100	100	1.1	29.6	71.4	100	0.0
Catalyst analyses[d]									
Sulphur (%)[e]	–	6.0	6.0	5.9	–	5.4	6.0	5.2	–
Carbon (%)	–	6.2	4.7	4.5	–	7.5	7.9	6.4	–
Methyl hexanoate									
Average conversion (%)	35.8	72.2	100	100	16.7	45.2	82.3	100	13.4
Hydrocarbon yield (%)[c]	6.5	45.9	100	100	1.1	27.1	64.0	100	0.0
Catalyst analyses[d]									
Sulphur (%)[e]	–	5.4	–	5.4	–	5.5	–	5.5	–
Carbon (%)	–	6.0	–	5.6	–	6.5	–	5.7	–

[a] Catalyst form.
[b] Temperature (°C).
[c] Yield $= \sum F_i/F_{e,in} \times 100\%$; where F_i is the molar flow rate of each hydrocarbon (mol/h) and $F_{e,in}$ the inlet molar flow rate of the ester (mol/h).
[d] Sulphur and carbon analysis of spent catalysts (presulphided catalysts: sulphur = 6.9% and carbon < 1% on the NiMo catalyst; sulphur = 7.0% and carbon < 1% on the CoMo catalyst).
[e] Sulphur content on carbon-free basis.

The repeated experiments with methyl heptanoate at 250 and 275 °C on the sulphided catalysts revealed that the experiments were well reproducible: the maximum variations in average ester conversions and hydrocarbon yields were ±3% from the average of the repeated tests. Molar balances based on liquid product analyses were calculated to be above 96%.

3.2. Thermal reactions and activity of the support and the oxide catalysts

Methyl heptanoate and methyl hexanoate did not react at 300 °C without catalysts. The alumina support converted about 13% of the esters at 300 °C and the identified products included only the alcohols and the acids. Although the alumina support had some activity for deesterification and dehydration reactions in accordance with its acidic nature [7], HDO does not appear to proceed on the alumina support.

The oxide NiMo catalyst exhibited more activity for the reactions of aliphatic methyl esters than the oxide CoMo catalyst (Table 1). Both catalysts produced all the identified products mentioned above. However, oxide NiMo produced mainly the alkenes and oxide CoMo yielded mainly *n*-heptane and heptenes from methyl heptanoate and *n*-hexane and hexenes from methyl hexanoate. Thus, unlike phenol and its derivatives [8,10], HDO of the aliphatic methyl esters proceeds to some extent on the non-sulphided catalysts.

3.3. Sulphided catalysts

Sulphidation greatly increased the activity of the catalysts, as seen in average ester conversions (Table 1). Nevertheless, the sulphided NiMo catalyst was more active than the sulphided CoMo catalyst. The conversion of both esters was complete at 275 °C on the sulphided NiMo catalyst and at 300 °C on the sulphided CoMo catalyst under the studied conditions. Comparison of the results with our earlier studies [4,8,9] showed that esters are clearly more reactive than phenolic compounds under similar hydrotreating conditions [2]. Alkanes were always the main products on the sulphided NiMo catalyst and alkenes were detected only at low conversions. On the other hand, alkanes were the main products only at 300 °C on the sulphided CoMo catalyst and alkenes were detected at all temperatures, although their amount decreased at complete conversions. The predominant formation of alkanes on the sulphided NiMo catalyst is consistent with its higher hydrogenation activity [6,7]. Alkanes were composed of mostly *n*-heptane from methyl heptanoate and *n*-hexane from methyl hexanoate under all conditions. Similarly, alkenes were mostly heptenes from methyl heptanoate and hexenes from methyl hexanoate on both sulphided catalysts. No oxygen-containing compounds were detected among the liquid products at complete conversions. Alcohols were detected in trace amounts only at incomplete conversions. In fact, high dehydration rates of alcohols have been reported under the conditions of hydrogenation by Weisser and Landa [7].

At incomplete conversions, the conversion of methyl heptanoate, and selectivity to hydrocarbons and 1-heptanol changed with time on stream on both sulphided catalysts (Fig. 1a and b). The molar ratio of C_7 to C_6 hydrocarbons increased from 1.0 to 1.5 on the NiMo and from 1.4 to 2.1 on the CoMo catalyst at 250 °C in 4 h. The molar ratio of *n*-heptane to heptenes decreased from 9.3 to 7.5 on the sulphided NiMo catalyst. In contrast, the ratio was constant at about 0.3 on the sulphided CoMo catalyst at this temperature. These changes in the product distribution were enhanced at higher temperatures, even though complete conversions of esters were achieved. The C_6 to C_5 hydrocarbon and the alkane to alkene ratios from methyl hexanoate also produced similar results. All these results indicate that the catalysts deactivated with time.

The carbon amount on the catalysts increased noticeably during the experiments and the sulphur amount decreased, as seen in Table 1. Thus, the carbon deposition and loss of active sites on the catalysts due to changing surface structure are likely reasons for the catalyst deactivation [11].

3.4. Reaction scheme

The variety of the products reveals that the reactions paths of methyl esters are composed of a number of parallel and consecutive reactions. The reaction scheme presented in Fig. 2 was suggested on the basis of identified reaction products. Hydrocarbons are produced from aliphatic methyl esters via three parallel reaction paths in which alcohols and carboxylic acids form intermediates. In path I, primary alcohols are produced from the esters through the hydrogenolysis of the C–O σ-bond of the carboxyl group. Dehydration of alcohols yields the alkenes and hydrogenation of alkenes leads to the corresponding alkane. In path II, the deesterification reaction yields carboxylic acids and methanol. The water required for the reaction may be supplied by the dehydration of the alcohols in path I. The formed carboxylic acids are either reduced to alcohol releasing a mole of water or decarboxylated to alkenes followed by hydrogenation to the corresponding alkane. Unlike decarboxylation, reduction of the carboxylic acid to the alcohol yields the same hydrocarbons with path I. Finally, path III is the direct decarboxylation of the esters to hexenes from methyl heptanoate and pentenes from methyl hexanoate. This path may also produce methane in addition to carbon dioxide.

A separate run with heptanoic acid was carried out at 250 °C in order to confirm the role of the acid proposed in the reaction scheme. Heptenes were the main products on the sulphided CoMo catalyst. Additionally, *n*-heptane, *n*-hexane, hexenes, 1-heptanol, methanol, methyl heptanoate and heptyl heptanoate were detected among the products. Reduction of heptanoic acid to 1-heptanol was followed by dehydration to heptenes, which were hydrogenated to
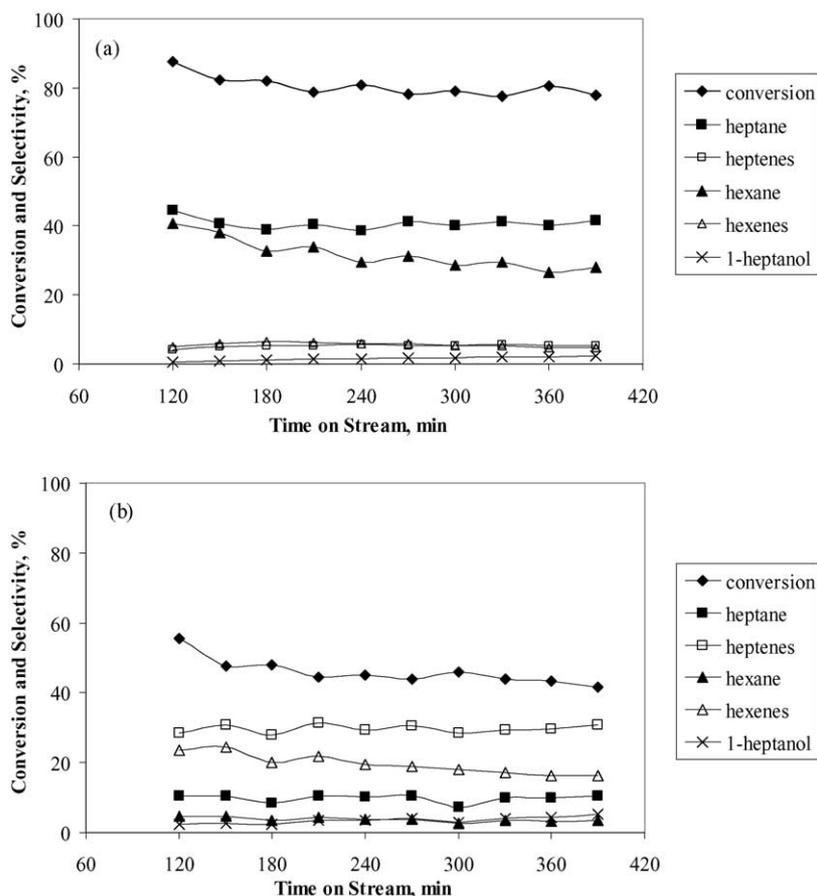
Fig. 1. Total conversion of methyl heptanoate, and selectivities to hydrocarbons and 1-heptanol on the sulphided (a) NiMo/γ-Al$_2$O$_3$ and (b) CoMo/γ-Al$_2$O$_3$ catalysts at 250 °C (heptenes: sum of 1-heptene, *cis*- and *trans*-2-heptene and 3-heptene; hexenes: sum of 1-hexene, *cis*- and *trans*-2-hexene and 3-hexene).

n-heptane. Decarboxylation of heptanoic acid produced hexenes and the hydrogenation of hexenes *n*-hexane, as indicated in Fig. 2. Thus, hydrocarbons formed about 60% of the products and the selectivity to heptenes was 38%. Selectivities to 1-heptanol and heptyl heptanoate were about 21 and 18%, respectively. It is worth noting that the formation of C$_6$ hydrocarbons ceased completely when the conversion of the heptanoic acid dropped from 71 only to 60%. Consequently, the carboxylic acid seems to be reduced mainly to alcohol on the sulphided CoMo catalyst followed by dehydration to hydrocarbons, as suggested in the reaction scheme. The formation of methanol can be explained with the hydrogenation of carbon oxides. In their study, Calafat et al. [12] reported the formation of alcohols via the hydrogenation of carbon dioxide on CoMo catalysts at 250–

300 °C under 3.0 MPa pressure. Formation of methyl heptanoate and heptyl heptanoate were attributed to the esterification reaction of heptanoic acid with methanol and 1-heptanol, respectively. This also explains the formation of heptyl heptanoate when methyl heptanoate was used as the feed at 250 °C. Selectivity to methyl heptanoate was about 2%. The low formation rate of the ester indicates that esterification of heptanoic acid with methanol is not significant under these conditions.

As a summary, the aliphatic methyl esters are converted to hydrocarbons via three main paths, which include decarboxylation steps and/or dehydration steps as well as hydrogenation steps. The dehydration steps produce the alkenes with the same number of carbon atoms as in the acyl group of the ester. The decarboxylation steps result in the
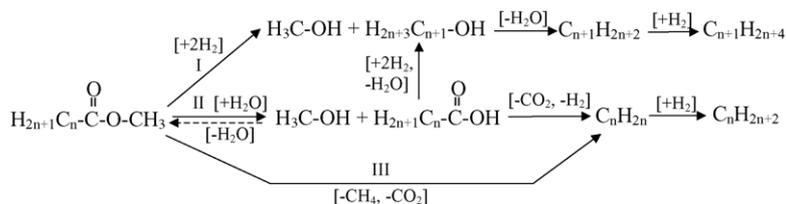

Fig. 2. Hydrodeoxygenation reaction scheme of aliphatic methyl esters ($n = 6$ for methyl heptanoate and $n = 5$ for methyl hexanoate).

alkenes with one carbon atom less than in the acyl group. The hydrogenation of the formed alkenes takes place following these deoxygenation steps.

The effect of deactivation on the deoxygenation steps can be evaluated with the ratio of C_7 to C_6 hydrocarbons formed from methyl heptanoate. The increase in this ratio with time indicates that the decarboxylation steps were deactivated faster than the dehydration steps. The difference was even more pronounced at higher temperatures. The cease of the formation of C_6 hydrocarbons in the test with heptanoic acid further supports the conclusion. Changes in the molar ratios of the alkane to the alkenes reveal the effect of deactivation on the hydrogenation step. However, no correlation was found between the deactivation of the deoxygenation steps and the hydrogenation steps. Furthermore, qualitatively, the results did not change with methyl hexanoate. From all observations, we tend to conclude that path III is the main route of decarboxylation to hydrocarbons from the aliphatic esters and the sites responsible for these reactions deactivate faster than those of dehydration steps leading to the hydrocarbons.

4. Conclusions

Methyl esters can be hydrodeoxygenated on sulphided hydrotreating catalysts under moderate conditions. The sulphided NiMo/γ-Al$_2$O$_3$ is more active catalyst than the sulphided CoMo/γ-Al$_2$O$_3$. HDO of the esters proceeds via a number of parallel and consecutive reactions. Hydrocarbons are formed as final products mainly from alcohol and/or carboxylic acid intermediates. Nevertheless, the stability of the catalysts was not satisfactory under the studied conditions as revealed in changes in the product distributions, even at complete conversions.

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