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Hydrodeoxygenation of methyl esters on sulphided NiMo/γ-Al_2O_3 and CoMo/γ-Al_2O_3 catalysts

O.İ. Şenol*, T.-R. Viljava, A.O.I. Krause

Laboratory of Industrial Chemistry, Helsinki University of Technology,
P.O. Box 6100, FIN-02015 Hut, Finland

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-Al_2O_3 and CoMo/γ-Al_2O_3 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.

Keywords: Bio-oil; Hydrodeoxygenation; HDO; Cobalt–molybdenum; Nickel–molybdenum; Methyl ester

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/Al_2O_3 and NiMo/Al_2O_3 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-Al_2O_3 and NiMo/γ-Al_2O_3 were tested with the model compounds methyl heptanoate and methyl hexanoate. HDO reaction schemes of the esters were presented.

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* Corresponding author. Tel.: +358 9 451 2625; fax: +358 9 451 2622.
E-mail address: ilke.senol@hut.fi (O.İ. Şenol).

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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_2O_3 and CoMo/γ-Al_2O_3 hydrotreatment catalysts in either oxide or sulphided form. Additionally, heptanoic acid (Aldrich, 99%) was used to study the reactions of a potential intermediate. Thermodynamic 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_2O_3 or CoMo/γ-Al_2O_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_2S/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_2O_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_2O_3				CoMo/γ-Al_2O_3				γ-Al_2O_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.