

# Hydrodeoxygenation 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> catalyst: The effect of water

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## Abstract

Water formed during hydrotreating of oxygen-containing feeds has been found to affect the performance of sulphided catalysts in different ways. The effect of water on the activity of sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in hydrodeoxygenation (HDO) of aliphatic esters was investigated in a tubular reactor by varying the amount of water in the feed. In additional experiments, H<sub>2</sub>S was added to the feed, alone and simultaneously with water.

Under the same conditions, the NiMo catalyst exhibited a higher activity than the CoMo catalyst. The ester conversions decreased with increase in the amount of added water. When H<sub>2</sub>S and water were added simultaneously, the conversion increased to the same level as without water addition on the NiMo catalyst and reached a higher value on the CoMo catalyst. The conversions were highest, however, when only H<sub>2</sub>S was added. Unfortunately, the conversions decreased with time under all conditions. On both catalysts, the total yield of the C<sub>7</sub> and C<sub>6</sub> hydrocarbons decreased with the amount of added water, while the concentrations of the oxygen-containing intermediates increased. The presence of H<sub>2</sub>S improved the total hydrocarbon yield and shifted the main products towards the C<sub>6</sub> hydrocarbons. Thus, the addition of H<sub>2</sub>S effectively compensated the inhibition by water.

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## 1. Introduction

Aliphatic fatty acid esters are produced from vegetable oils via transesterification [1–3]. Fatty acid methyl esters, which are the products of transesterification of triglycerides with methanol, are a promising alternative fuel for diesel engines [4]. Known as biodiesel, these esters can be upgraded by hydrodeoxygenation (HDO) to improve fuel properties and to obtain synthetic biofuels. In HDO on sulphided catalysts similar to those used for hydrosulphurisation in oil refineries, oxygen is removed in the form of water [5]. Like the organic oxygen-containing compounds, water produced in HDO may affect the activity, stability and selectivity of the sulphided catalysts by modifying the catalyst surface [5,6]. Since the sulphur content of biodiesel is typically very low (<0.002 wt%) [1],

addition of a sulphiding agent, such as H<sub>2</sub>S, may be required to maintain the sulphidation level of the catalyst during hydrotreating.

Contradictory conclusions on the effect of water have been presented in several HDO studies reported in the literature. In a study on HDO of dibenzofuran on a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst under 6.9 MPa total pressure, La Vopa and Satterfield [7] found that 24 kPa partial pressure of water did not affect the HDO rate in the presence of H<sub>2</sub>S but accelerated the rate in the absence of H<sub>2</sub>S. On the other hand, Vogelzang et al. [8] observed inhibition of 1-naphthol HDO on sulphided Mo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts by water formed in the reactions. In more recent work comparing the effects of water, H<sub>2</sub>S and ammonia, Laurent and Delmon [9,10] reported that the addition of water caused only weak inhibition of HDO of ketones, carboxylic compounds and phenol on NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. In another study [11], Laurent and Delmon observed that 2.5 MPa partial pressure of water

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was responsible for the loss of two-thirds of the initial activity of a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst in 60 h during HDO of a mixture of substituted phenols under 7 MPa total pressure. Characterisation of the catalyst with XPS revealed a modification in the catalyst structure by water: partial crystallisation of  $\gamma$ -alumina support into a hydrated boehmite phase but no change in the metal content, dispersion or sulphidation state [11].

We sought a deeper understanding of the effect of water on catalyst performance in HDO with a view to optimising the process conditions. Contradictory results from different HDO studies on the effect of water indicate that various HDO reactions are affected differently by water. Recently, we studied HDO reactions of aliphatic methyl esters on NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts [12]. In the present work, using the same catalysts, we focus on the effect of water on the catalyst performance.

## 2. Experimental

NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were commercial hydrotreating catalysts containing 1–5 wt% promoter and 10–20 wt% active metal. The catalyst (0.59–0.75 mm, 0.5 g) was placed between two layers of silicon carbide (1–3 mm) in a tubular continuous flow reactor made of stainless steel (i.d. 10 mm, length 380 mm). Activation of the catalyst was carried out at 400 °C under atmospheric pressure as follows: 2 h calcination under nitrogen (AGA, 99.999%) flow at a rate of 2.5 l/h (NTP) followed by 4 h presulphidation under 5 vol% H<sub>2</sub>S/H<sub>2</sub> gas mixture (AGA, 99.999%) flow at a rate of 2.5 l/h (NTP).

Experiments were carried out at 250 °C under 1.5 MPa total pressure. Hydrogen (AGA, 99.999%) was passed through a gas bubbler filled with distilled water, located upstream of the reactor. The temperature of the bubbler was controlled with a heater and the amount of water fed to the reactor, calculated from saturated vapour pressure of water, was 750, 1800, 5000 or 18,600 ppm. Additional experiments were carried out by adding 830 ppm H<sub>2</sub>S and 18,600 ppm water simultaneously or 1000 ppm H<sub>2</sub>S alone. Total gas flow rate during the runs was set to 2.0 l/h (NTP). The liquid feed contained 3 wt% methyl heptanoate (Fluka Chemika, >99%) or ethyl heptanoate (Aldrich, 99%) in *m*-xylene (Fluka Chemika, >98%) and was fed at a rate of 10 g/h. Sampling was started after a 2 h stabilisation period and repeated every 30 min.

Liquid samples were analysed with a Hewlett-Packard gas chromatograph (HP 6890, flame ionisation detector, HP-1 column). The gas phase was analysed qualitatively with an online gas chromatograph (HP 5890A, thermal conductivity detector, packed column of activated carbon with 2% squalane).

Sulphur and carbon contents of the catalyst samples after the reactions were determined with a LECO analyser (SC-444 series).

## 3. Results and discussion

### 3.1. General remarks

Comparison of conversion values and hydrocarbon yields of repeated experiments showed the experiments to be highly reproducible: conversion values and hydrocarbon yields were within  $\pm 2\%$  units. Molar balances based on the liquid product analyses were calculated to be about 95% on average. Thermodynamic calculations predicted that the reactant and products are in gas phase under the studied conditions.

Because of low solubility of water in *m*-xylene, water could not be added to the liquid feed directly. The amount of water fed to the reactor was limited by the saturated vapour pressure. The highest concentration of water in the feed was 0.6 wt%, corresponding to a water to ester molar ratio of 1.6. Note that water formed in reactions further added to the total water concentration in the reactor.

### 3.2. Catalytic activities

In all experiments, the ester conversions decreased with time, indicating the deactivation of the catalyst. These decreases were about 10% units in 4 h. Comparability was ensured by calculating all conversion and yield values after 3 h on stream. Before the reactions, the sulphur content of the sulphided catalysts was measured to be about 6.9 wt%. Except for the experiments with the NiMo catalyst where H<sub>2</sub>S was added alone, the sulphur content of the catalysts decreased during the reactions: the sulphur content of the NiMo catalyst dropped to 6.0 wt% on carbon-free basis and that of the CoMo catalyst to 5.0 wt%. Meanwhile, the carbon content of the catalysts increased up to 6.3 wt% on the NiMo catalyst and to 7.5 wt% on the CoMo catalyst. The losses in the sulphur content and the significant increases in the carbon content during the reactions are at least partially responsible for the deactivation with time. Similar observations have been reported earlier [5,6].

Fig. 1 shows the conversions of methyl heptanoate after 3 h. Higher ester conversions on the NiMo catalyst revealed its better activity than the CoMo catalyst. The ester conversion decreased as a function of added water concentration, indicating an inhibition by water. For instance, without any water addition, the conversion of methyl heptanoate on the NiMo catalyst was 82% after 3 h (Fig. 1). From the selectivities and the proposed reaction scheme [12], the concentration of water in the product was estimated to be about 8600 ppm. The conversion decreased to 69% with 18,600 ppm added water (24,800 ppm total water concentration in the reactor). Similarly, the conversion dropped from 48 to 41% on the CoMo catalyst.

The presence of H<sub>2</sub>S enhanced catalyst activities. The highest conversions, about 87% on the NiMo catalyst and about 65% on the CoMo catalyst after 3 h, were obtained in the presence of H<sub>2</sub>S when no water was added. When

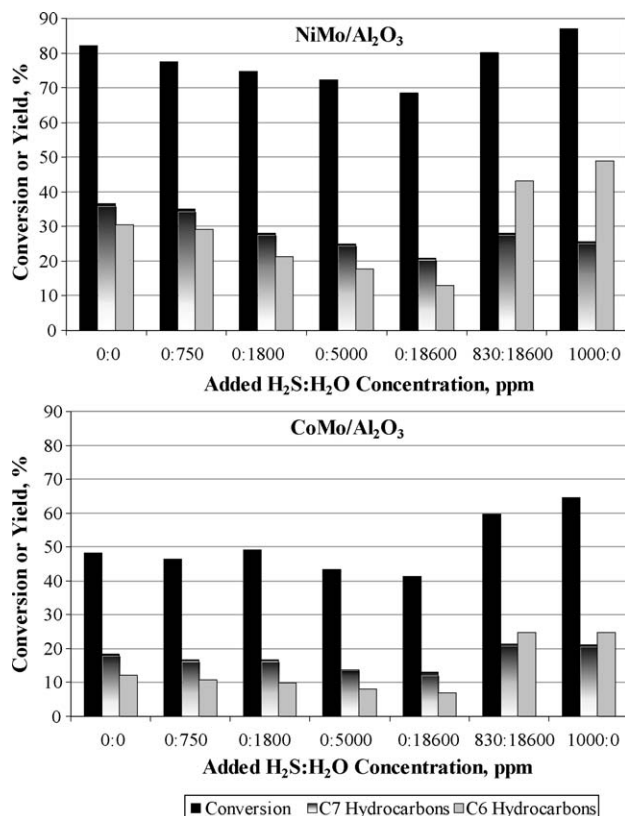


Fig. 1. Conversion of methyl heptanoate and hydrocarbon yields after 3 h.

H<sub>2</sub>S and water were added simultaneously, the ester conversion on the NiMo catalyst increased to the level achieved when no water was added, and on the CoMo catalyst it reached even a higher value (Fig. 1). Evidently, the added H<sub>2</sub>S was sufficient to compensate the inhibiting effect of water. The same conversion trends were found with ethyl heptanoate.

### 3.3. Product distribution

On both catalysts, the final products were hydrocarbons: heptane, hexane and some isomers of heptene and hexene. Heptanol, heptanoic acid and heptyl heptanoate were detected as oxygen-containing compounds formed from the two esters. In addition, methanol from methyl heptanoate and ethanol and diethyl ether from ethyl heptanoate were identified in the liquid samples. The gas phase analyses revealed the formation of CO<sub>2</sub> and CO in the reactions,

indicating additional removal of oxygen in the form of carbon oxides. Methane was detected in the gas phase analyses when methyl heptanoate was used as the feed.

Heptanol and heptanoic acid were assumed to be primary products in the reaction scheme presented in our previous paper [12]. Fig. 2 depicts a simplified reaction scheme for methyl heptanoate. Dehydration of heptanol to the C<sub>7</sub> hydrocarbons and decarboxylation of methyl heptanoate and heptanoic acid to the C<sub>6</sub> hydrocarbons can be described in terms of deoxygenation reactions that are followed by hydrogenation reactions. Heptyl heptanoate is a side product formed via esterification of the intermediates heptanol and heptanoic acid. With ethyl heptanoate used as the feed, the methanol in Fig. 2 should be replaced with ethanol. The formation of diethyl ether can be explained in terms of the dehydration of ethanol [13]. A corresponding formation of dimethyl ether from methanol would be expected, but it could not be detected in the liquid samples owing to its high volatility and low boiling point. The gas chromatograph used for analysis of the gas phase was also unable to detect dimethyl ether. Ethane, which should be produced from the alkyl part of ethyl heptanoate, like methane from methyl heptanoate, could not be separated with the column used in the gas chromatograph analyses.

The amount of hydrocarbons was always higher on the NiMo catalyst than on the CoMo catalyst. In addition, under all conditions the NiMo catalyst was more selective to the saturated hydrocarbons. This result is in good agreement with the higher hydrogenation capacity of the NiMo catalyst than the CoMo catalyst [14]. In the absence of H<sub>2</sub>S, heptane and heptenes were the main products on the NiMo and CoMo catalysts, respectively. When H<sub>2</sub>S was added alone or simultaneously with water, hexane and hexenes were the main products on the NiMo and CoMo catalysts, respectively.

The yields of C<sub>7</sub> and C<sub>6</sub> hydrocarbons produced from methyl heptanoate are presented in Fig. 1. On both catalysts, the yields decreased as a function of added water concentration. On the NiMo catalyst, the decrease was especially marked for heptane and hexane. As a result and as seen in Table 1, the molar ratio of saturated to unsaturated hydrocarbons dropped with the addition of water. These results suggest that the added water suppresses the hydrogenation reactions on the NiMo catalyst. The addition of H<sub>2</sub>S alone or simultaneously with water also decreased these ratios, indicating the inhibition of hydrogenation reactions in the presence of H<sub>2</sub>S, too. On the CoMo catalyst,

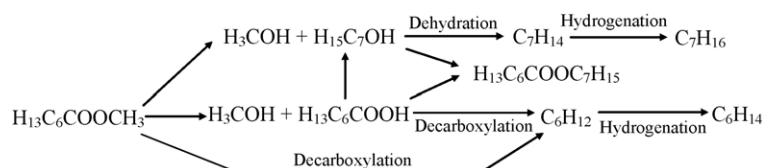


Fig. 2. HDO reaction scheme of methyl heptanoate.

Table 1  
Molar ratios of hydrocarbons from methyl heptanoate after 3 h

Added H <sub>2</sub> S:H <sub>2</sub> O concentration (ppm)	NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>			CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		
	Heptane/Heptenes <sup>b</sup>	Hexane/Hexenes <sup>b</sup>	C <sub>7</sub> /C <sub>6</sub> <sup>b</sup>	Heptane/Heptenes <sup>b</sup>	Hexane/Hexenes <sup>b</sup>	C <sub>7</sub> /C <sub>6</sub> <sup>b</sup>
0:0 <sup>a</sup>	8.8	5.7	1.2	0.3	0.2	1.5
0:750	7.2	3.3	1.2	0.4	0.2	1.6
0:1800	6.2	3.7	1.3	0.4	0.2	1.7
0:5000	5.4	3.1	1.4	0.4	0.3	1.7
0:18600	4.6	2.8	1.6	0.3	0.2	1.9
830:18600	2.9	1.6	0.7	0.3	0.2	0.9
1000:0	1.8	1.2	0.5	0.3	0.2	0.9

<sup>a</sup> From ref. [12].

<sup>b</sup> Molar ratios (mol/mol).

the ratios were about 0.3 for the C<sub>7</sub> hydrocarbons and 0.2 for the C<sub>6</sub> hydrocarbons under all conditions studied (Table 1). Hence, no significant effect of H<sub>2</sub>S and water on the hydrogenation reactions was apparent on the CoMo catalyst. On both catalysts, the addition of water decreased the yield of C<sub>6</sub> hydrocarbons more than the yield of C<sub>7</sub> hydrocarbons and the C<sub>7</sub> to C<sub>6</sub> hydrocarbon molar ratios increased as a result (Table 1). Evidently, the added water mainly suppresses the decarboxylation reactions on the catalysts. Compared with the yield without water addition, the addition of H<sub>2</sub>S alone and simultaneously with water improved the C<sub>6</sub> hydrocarbon yield in particular (Fig. 1). Accordingly, the C<sub>7</sub> to C<sub>6</sub> hydrocarbon ratios decreased significantly (Table 1). These decreasing hydrocarbon ratios indicate that the addition of H<sub>2</sub>S clearly enhances the decarboxylation reactions on the catalysts.

On both catalysts, the yields of the oxygen-containing intermediates, i.e. heptanol and heptanoic acid, increased with the concentration of added water. When 18,600 ppm water was added, the heptanol yield on the NiMo catalyst was more than doubled and the yield of heptanoic acid increased by about one-third relative to the situation when no water was added. Correspondingly, on the CoMo catalyst, the heptanol yield was doubled and the yield of heptanoic acid was increased by about two-thirds. In all cases of H<sub>2</sub>S addition, the yield of heptanol was decreased relative to the yield with no addition of water or H<sub>2</sub>S. It is noteworthy that the yields of heptanol and heptanoic acid did not exceed 5 and 10%, respectively, in any experiment. The yield of heptyl heptanoate varied in parallel with the heptanol and heptanoic acid yields since it is the product of these oxygen-containing compounds. The amount was always less than 5%. Ethyl heptanoate produced similar results. Diethyl ether always represented less than 2 wt% of the products and it decreased with the addition of H<sub>2</sub>S and water.

#### 4. Conclusions

The activity of the sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the HDO of aliphatic fatty acid esters is higher than that

of the sulphided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Water inhibits both catalysts. It decreases the conversion of the esters and suppresses the oxygen removal reactions on the catalysts. Hydrogenation reactions are, however, inhibited on the NiMo catalyst by water but not affected on the CoMo catalyst. Comparison of the two deoxygenation reactions, i.e. dehydration and decarboxylation, showed that water mainly affects the decarboxylation reactions, suppressing the formation of C<sub>6</sub> hydrocarbons. The addition of H<sub>2</sub>S effectively compensates the inhibition by water but also changes the product distribution: it shifts the main products towards the C<sub>6</sub> hydrocarbons. This may be a drawback since the production of carbon oxides increases accordingly.

Since water is always present in the reactor during HDO of aliphatic fatty acid esters on sulphided catalysts, a sulphiding agent must be added to the reactor to maintain catalyst activity. The amount of H<sub>2</sub>S needs to be optimised for the desired activity of the catalyst and the target product quality.

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