

# Reactions of methyl heptanoate hydrodeoxygenation on sulphided catalysts

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Received 10 November 2006; received in revised form 4 December 2006; accepted 5 December 2006

Available online 9 December 2006

## Abstract

Reactions of methyl heptanoate on sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in gas and liquid phases were investigated in detail. Experiments with heptanol and heptanoic acid were carried out in support of the conclusions. Hydrodeoxygenation (HDO) of the ester produced C<sub>7</sub> and C<sub>6</sub> hydrocarbons. Alcohols, aldehyde, carboxylic acid and ethers were formed as intermediates. In addition, a few sulphur-containing compounds were formed as intermediates and they led to desulphurisation of the catalysts. The reactions of the ester and the intermediates are explained in terms of hydrogenation and acid-catalysed reactions such as hydrolysis, esterification and dehydration. The E<sub>2</sub> elimination and S<sub>N</sub>2 nucleophilic substitution mechanisms are proposed to play a role in the reactions. HDO and hydrogenation activities were higher on the NiMo catalyst than the CoMo catalyst. The NiMo catalyst might thus seem to be preferred for the conversion of aliphatic esters, alcohols and carboxylic acids. According to the proposed reaction scheme, however, hydrogen consumption will be greater with this catalyst.

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**Keywords:** Hydrodeoxygenation; Sulphided catalyst; Bio-oil; Hydrotreating; Aliphatic ester

## 1. Introduction

Wood-based bio-oil is a renewable alternative fuel suitable for the replacement of fossil fuels. When wood-based bio-oil is used as fuel, atmospheric carbon is merely recycled, unlike fossil fuels whose fixed carbon is mobilised and adds to the atmospheric pool [1–3]. Thus, bio-oil is considered as CO<sub>2</sub> neutral even though the method of producing it may require hydrogen, the production of which yields CO<sub>2</sub>. A further positive feature of wood-based bio-oil is that the sulphur content is negligible and the nitrogen content is low, so that bio-oil generates less SO<sub>x</sub> and NO<sub>x</sub> emissions than fossil fuels [1,2,4,5]. The oxygen content of bio-oil is high, however (35–50 wt%). The amount and type of oxygen-containing compounds depend on the biomass source and the bio-oil production conditions. Oxygen is present as alcohols, carboxylic acids, aldehydes, esters, ketones, phenols, sugars, furans and many other oxygenates [1,2,5].

The high oxygen content of bio-oil induces thermal and chemical instability, immiscibility with hydrocarbon fuels and

low heating value as compared with hydrocarbon fuels [2,4]. Bio-oil as such cannot be utilised as motor fuel, therefore. The necessary upgrading of bio-oil, in which the oxygen content is reduced, can be achieved by hydrodeoxygenation (HDO), which entails the elimination of oxygen and the formation of hydrocarbons in the presence of hydrogen on sulphided hydroprocessing catalysts. The typical catalysts, such as NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>, are active in sulphided form, but the oxygen-containing compounds present in bio-oil may modify the sulphide structure causing a loss of catalytic performance [5].

The HDO reactivity of bio-oil varies with the source, according to the type and amount of oxygen-containing compounds. HDO of the oxygen-containing compounds present in bio-oil needs to be thoroughly investigated for a full understanding and reliable optimisation of the upgrading process conditions, most notably hydrogen consumption. Several studies on the HDO of phenolic and furanic compounds are reported in literature [5] but only a few on the HDO of aliphatic diethyl esters in the reaction mixture [6–11]. In a recent study of the HDO of aliphatic methyl esters on NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in a fixed-bed flow reactor [12,13], we found that the HDO of methyl esters produces hydrocarbons as the final products, and

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oxygen-containing compounds are formed as intermediates. In the present study, we deepen our understanding of the reaction paths of the HDO of aliphatic esters. Methyl heptanoate was used as model ester compound. Additional experiments with heptanol and heptanoic acid were performed to explore the role of these oxygen-containing compounds in the reaction paths. Possible reaction mechanisms and catalyst active sites are discussed.

## 2. Experimental

Experiments were carried out in gas phase in a tubular fixed-bed flow reactor and in liquid phase in a batch reactor. The reaction mixture contained methyl heptanoate (Fluka Chemika, >99%, or Merck, >98%), 1-heptanol (Aldrich, 98%) or *n*-heptanoic acid (Aldrich, 99%) in *m*-xylene (Merck, >99%). *n*-Decane (Sigma, >99%) was added as an internal standard in the batch reactor experiments. The chemicals were confirmed to be water-free by NMR analysis. Nitrogen, hydrogen and 5 vol% H<sub>2</sub>S/H<sub>2</sub> mixture were obtained with 99.999% purity from AGA.

Experiments in the flow reactor were performed with commercial NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and CoMo/γ-Al<sub>2</sub>O<sub>3</sub> hydrotreating catalysts. The batch reactor experiments were carried out only with the NiMo catalyst. Both catalysts were crushed and sieved to a fraction of 0.59–0.75 mm.

### 2.1. Experiments in the flow reactor

The flow reactor was made of stainless steel (i.d. 10 mm and length 380 mm). It was heated with an electrical furnace and the temperature was monitored with a thermocouple in the reactor. The liquid outlet stream of the reactor was withdrawn through a sampling vessel, which was cooled in an ice bath.

Experiments were carried out isothermally at 250 °C under 1.5 MPa pressure. In the experiments with the ester and acid, the liquid feed contained 3 wt% methyl heptanoate or heptanoic acid in *m*-xylene and the catalyst amount was 0.5 g. In the experiments with heptanol, the amounts of the alcohol and catalysts varied as set out in Table 1. Flow rate of the liquid feed was 10 g/h in all experiments and that of the gas feed, which contained pure hydrogen, 2 l/h (NTP). Details of the catalyst pretreatment and reaction procedure can be found in our previous paper [12]. A

standard run continued for 6.5 h. Catalyst deactivation was studied with methyl heptanoate, separately, in experiments of 15 h on stream. A further run was carried out to determine possible reactions of methyl heptanoate in the absence of a catalyst.

### 2.2. Experiments in the batch reactor

The batch reactor was a 50-ml autoclave equipped with a fixed-catalyst basket and a magnetic stirrer. In all experiments, the mixing speed was kept constant at 1000 rpm during the pretreatment and reaction.

A batch of NiMo/γ-Al<sub>2</sub>O<sub>3</sub> catalyst (0.5 g) was packed into the catalyst basket. After the catalyst was calcined for 2 h at 350 °C under 6 l/h (NTP) nitrogen flow, a 2 h presulphidation period was initiated by changing the nitrogen flow to 5 vol% H<sub>2</sub>S/H<sub>2</sub> gas mixture at a rate of 3 l/h (NTP). Experiments at 250 °C under 7.5 MPa hydrogen pressure were started by the addition of 16 ml reaction mixture containing 5 wt% methyl heptanoate, 2 wt% heptanol or 2 wt% heptanoic acid and 1 wt% *n*-decane in *m*-xylene. The reaction time in the experiments was varied between 5 and 180 min. Before each sample (about 100 mg) was removed, the sampling line was purged with about 250 mg of the reaction mixture. No hydrogen was added to the reactor during the runs and the number of samples was limited to 5 in each run in order to avoid a pressure and volume drop due to the sampling. Hence, the vapour–liquid phase equilibrium was assumed not to be affected by a pressure change in the reactor. The results are discussed on the basis of the liquid phase compositions. Possible reactions of the methyl ester in the absence of a catalyst in the liquid phase were studied separately.

### 2.3. Analysis

The liquid samples were analysed with a Hewlett-Packard gas chromatograph (HP 6890 Series) equipped with an HP-1 column (60 m × 0.25 mm × 1 μm film thickness) and a flame ionisation detector. The response factors for the reactants and the products were determined and checked regularly with calibration solutions of known concentrations. A few liquid samples were analysed qualitatively by GC/MS for the identification of trace compounds. The gas outlet stream of the flow reac-

Table 1  
Reaction of heptanol on sulphided NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and CoMo/γ-Al<sub>2</sub>O<sub>3</sub> catalysts in the flow reactor

| Exp. | Heptanol (wt%) | Catalyst and amount (g)               |                                       | Conversion (%)     |                  | Selectivity (%) |          |                | Catalyst (wt%) |                |
|------|----------------|---------------------------------------|---------------------------------------|--------------------|------------------|-----------------|----------|----------------|----------------|----------------|
|      |                | NiMo/γ-Al <sub>2</sub> O <sub>3</sub> | CoMo/γ-Al <sub>2</sub> O <sub>3</sub> | Total <sup>a</sup> | HDO <sup>b</sup> | Heptane         | Heptenes | Diheptyl ether | S <sup>c</sup> | C <sup>d</sup> |
| Al-1 | 3              | 0.5                                   | –                                     | ~100               | ~100             | 100             | –        | –              | 7.1            | 4.6            |
| Al-2 | 3              | 0.3                                   | –                                     | ~100               | ~100             | 100             | –        | –              | 7.0            | 5.4            |
| Al-3 | 6              | 0.3                                   | –                                     | ~100               | ~100             | 94              | 5        | 1              | 6.8            | 5.9            |
| Al-4 | 10             | 0.3                                   | –                                     | 93                 | 92               | 90              | 9        | 1              | 7.0            | 5.6            |
| Al-5 | 15             | 0.2                                   | –                                     | 56                 | 51               | 65              | 26       | 9              | 6.9            | 5.6            |
| Al-6 | 3              | –                                     | 0.5                                   | ~100               | ~100             | 75              | 24       | 1              | 5.9            | 5.8            |
| Al-7 | 6              | –                                     | 0.3                                   | 82                 | 75               | 34              | 58       | 8              | 5.6            | 7.3            |

<sup>a</sup> Total heptanol conversion.

<sup>b</sup> Conversion to hydrocarbons.

<sup>c</sup> Carbon-free sulphur content of the catalyst after the reactions (7.0 ± 0.3 wt% sulphur before the reactions).

<sup>d</sup> Carbon content of the catalyst after the reactions.

tor was qualitatively analysed with an online Hewlett-Packard gas chromatograph (HP 5890A, thermal conductivity detector, HP-PLOT/U column of dimensions 30 m × 0.32 mm and 10 μm film thickness). At the end of the experiments, the gas phase of the batch reactor was probed for CO<sub>2</sub>, CO and H<sub>2</sub>S with Dräger tubes.

Sulphur and carbon contents of the catalysts were determined after the experiments with a sulphur and carbon analyser (LECO, Series SC-444).

#### 2.4. Calculations

Total conversion of the reactant,  $X_A$ , and the selectivity to product  $i$ ,  $S_i$ , were defined by

$$X_A = \frac{F_{A,\text{in}} - F_{A,\text{out}}}{F_{A,\text{in}}} \times 100\% \quad (1)$$

$$S_i = \frac{F_i}{F_{A,\text{in}} - F_{A,\text{out}}} \times 100\% \quad (2)$$

where  $F_{A,\text{in}}$  and  $F_{A,\text{out}}$  are the inlet and outlet molar flows of the reactant (mol/h), respectively, and  $F_i$  is the molar flow of the product  $i$  (mol/h). In the batch reactor experiments, conversions and selectivities were calculated from the number of moles of the reactant and products. HDO conversion was defined as the fraction of the reactant converted to hydrocarbons.

### 3. Results

Repeated experiments in both the flow and the batch reactors showed that the conversion and selectivity values varied by ±2%, indicating good reproducibility of the experimental data. The separate reactions of methyl heptanoate, heptanol and heptanoic acid in the flow and batch reactors are examined in the following.

#### 3.1. Reactions of methyl heptanoate

In experiments in the flow reactor, total conversion of methyl heptanoate, on both catalysts, reached a pseudo steady state after about 10% units decrease in 4 h (Fig. 1). Accord-

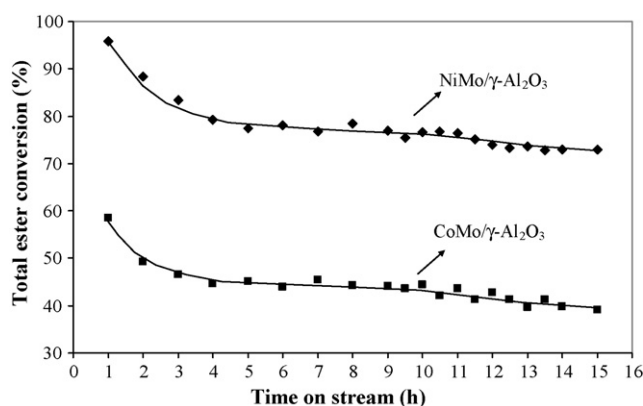


Fig. 1. Conversion of methyl heptanoate on sulphided NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and CoMo/γ-Al<sub>2</sub>O<sub>3</sub> catalysts at 250 °C under 1.5 MPa in the flow reactor.

ingly, later in this paper, conversions and selectivities are compared using the average values calculated between 4 and 6.5 h. Total conversion of the ester at steady state was about 78% on the NiMo catalyst and 46% on the CoMo catalyst. In addition to the hydrocarbons, alcohol, carboxylic acid and ester-type compounds reported previously [12,13], the GC/MS analysis in the present work uncovered a group of minor oxygen-containing and sulphur-containing products. The reaction products in the liquid samples were identified as heptane, 1-heptene, *cis/trans*-2-heptene, *cis/trans*-3-heptene, hexane, 1-hexene, *cis/trans*-2-hexene, *cis/trans*-3-hexene, heptanal, 1-heptanol, methanol, *n*-heptanoic acid, heptyl heptanoate, dimethyl ether, diheptyl ether, 1-methanethiol, 1-hexanethiol, 1-heptanethiol, dimethyl sulphide, diheptyl sulphide and dissolved H<sub>2</sub>S. In this paper, heptenes and hexenes are referred to as unsaturated hydrocarbons. Carbon oxides (CO and CO<sub>2</sub>) and methane were found in the analysis of the gas outlet stream. Hydrocarbons, heptanol, heptanoic acid and heptyl heptanoate dominated the products in the liquid samples (Fig. 2). The HDO conversion of the ester was 67% on the NiMo catalyst and 34% on the CoMo catalyst. The NiMo catalyst was selective for the saturated hydrocarbons and the CoMo catalyst for the unsaturated hydrocarbons (Fig. 2). The NiMo catalyst produced heptane with a selectivity of 43% and the CoMo catalyst heptenes with a selectivity of 35% as the main products. Sulphur-containing compounds were scarcely detected in the analyses suggesting that they were formed in trace amounts.

In the experiments in the batch reactor, complete conversion of methyl heptanoate was achieved in 2.5 h and complete HDO in 3 h. The products identified in the liquid samples were the same as those found in the flow reactor experiments. In addition, the qualitative analysis of the gas phase after the reactions showed the presence of CO, CO<sub>2</sub> and H<sub>2</sub>S. Concentrations of the major products (i.e. hydrocarbons, heptanol, heptanoic acid and heptyl heptanoate) in the reaction mixture changed as a function of time, as seen in Fig. 3. The concentrations of heptane and hexane nearly stabilised after 2.5 h. Unsaturated hydrocarbons totally vanished within 3 h. The concentrations of heptanol and heptyl heptanoate increased with time, as seen in Fig. 3, but, in a longer run, they decreased when the ester conversion was complete. Total ester conversion reached 10% in the first 1 min. At this

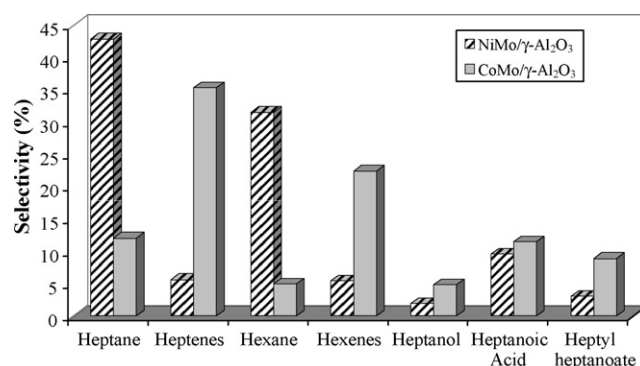


Fig. 2. Product distribution for reactions of methyl heptanoate on sulphided NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and CoMo/γ-Al<sub>2</sub>O<sub>3</sub> catalysts at 250 °C under 1.5 MPa pressure in the flow reactor.

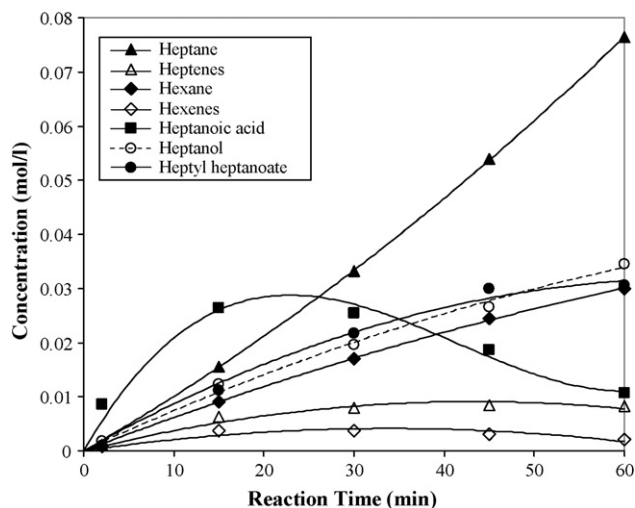


Fig. 3. Concentrations of products formed in the reactions of methyl heptanoate on sulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 250 °C under 7.5 MPa pressure in the batch reactor.

conversion level, the concentration of acid was about five times the amount of other products and it decreased after the ester conversion reached 60%.

Study of reactions in the flow reactor in the absence of a catalyst revealed the formation of heptanol and methanol. Similarly, heptanol, heptanoic acid and methanol were detected in the absence of a catalyst in the batch reactor. However, the ester conversions in 1 h reaction time did not exceed 5% in either reactor.

The sulphur content of the presulphided NiMo and CoMo catalysts was  $7.0 \pm 0.3$  wt% before the experiments in the flow reactor. Sulphur content of the NiMo catalyst in the batch reactor was about  $5.8 \pm 0.3$  wt%. As can be seen in Table 2, the carbon-free sulphur content of both catalysts decreased during the reactions in the flow reactor, but no significant change in the sulphur content of the catalyst took place in the batch reactor. The carbon content of the catalysts increased up to 7.5 wt% during the reactions in the flow and batch reactors (Table 2).

### 3.2. Reactions of 1-heptanol

Table 1 shows heptanol conversions with different catalyst loadings and amounts of reactant in the flow reactor. When the reactions were carried out on the NiMo catalyst, the alcohol

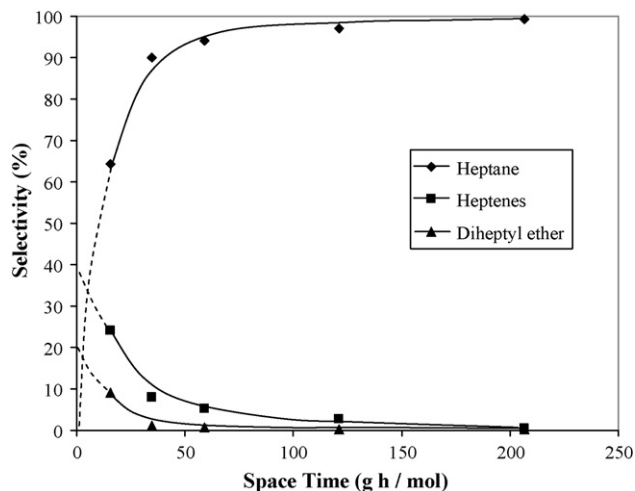


Fig. 4. Product distribution for reactions of heptanol at various space times in the flow reactor.

conversion was complete under the conditions of experiments Al-1, Al-2 and Al-3. Because the conversion was complete, further experiments were carried out with catalyst loadings or amounts of heptanol that led to incomplete conversions, allowing the detection of reaction intermediates. These experiments revealed the formation of diheptyl ether and the same C<sub>7</sub> hydrocarbons as in the reactions of methyl heptanoate. 1-Heptanethiol and diheptyl sulphide were identified as the sulphur-containing compounds. Analysis of the gas outlet stream of the flow reactor did not reveal any gaseous products. The selectivities to heptane, heptenes and diheptyl ether, are presented in Fig. 4 at various space times, where space time is defined as the ratio of the amount of catalyst to the molar flow of heptanol. Under all the conditions studied the main product on the NiMo catalyst was heptane. At 93% total conversion level the selectivity to heptane was 90%, and at 56% conversion level it was 64% (Table 1). On the CoMo catalyst, the conversion of heptanol was complete under the conditions of experiment Al-6 and the selectivity to heptane was 75%. At incomplete conversion level (experiment Al-7), heptenes were the main products and the catalyst selectivity to them was 58%.

Except for diheptyl sulphide, the products in the liquid samples in the batch reactor experiments were the same as those detected in the flow reactor experiments. Heptanol produced mostly unsaturated and saturated C<sub>7</sub> hydrocarbons. Diheptyl ether was formed in trace amounts. Heptanol conversion was

Table 2  
Sulphur and carbon contents (wt%) of catalysts after experiments in the flow and batch reactors with methyl heptanoate, 1-heptanol and *n*-heptanoic acid as reactant

|                            | Methyl heptanoate |     |                |     | 1-Heptanol     |                |                |                | <i>n</i> -Heptanoic acid |     |                |     |
|----------------------------|-------------------|-----|----------------|-----|----------------|----------------|----------------|----------------|--------------------------|-----|----------------|-----|
|                            | NiMo              |     | CoMo           |     | NiMo           |                | CoMo           |                | NiMo                     |     | CoMo           |     |
|                            | S <sup>a</sup>    | C   | S <sup>a</sup> | C   | S <sup>a</sup> | C              | S <sup>a</sup> | C              | S <sup>a</sup>           | C   | S <sup>a</sup> | C   |
| Flow reactor               | 6.0               | 6.2 | 5.4            | 7.5 | – <sup>c</sup> | – <sup>c</sup> | – <sup>c</sup> | – <sup>c</sup> | 5.7                      | 7.7 | 4.9            | 8.9 |
| Batch reactor <sup>b</sup> | 5.6               | 5.7 | –              | –   | 5.7            | 2.3            | –              | –              | 5.3                      | 2.7 | –              | –   |

<sup>a</sup> Sulphur content of the catalyst on carbon-free basis (before the reactions  $7.0 \pm 0.3$  wt% in the flow reactor and  $5.8 \pm 0.3$  wt% in the batch reactor).

<sup>b</sup> Sulphur and carbon contents after 1 h reaction time.

<sup>c</sup> Reported in Table 1.

complete in 45 min and only heptane was detected in the reaction mixture.

As seen in Table 1, in the flow reactor experiments with heptanol, the carbon-free sulphur content of the NiMo catalyst was more or less maintained during the reactions, but that of the CoMo catalyst dropped to below 6.0 wt%. Meanwhile, the carbon content increased. In the batch reactor experiments, the sulphur of the NiMo catalyst decreased slightly while the carbon content increased (Table 2).

### 3.3. Reactions of *n*-heptanoic acid

As with methyl heptanoate, total conversion of heptanoic acid in the flow reactor changed with time on stream. At pseudo steady state, total acid conversions were about 90% on the NiMo catalyst and 47% on the CoMo catalyst, while the HDO conversions were 82% on the former and 34% on the latter catalyst. The products in the liquid samples were heptanal, 1-heptanol, heptyl heptanoate, diheptyl ether, 1-hexanethiol, 1-heptanethiol and the same hydrocarbons as detected in the reactions of methyl heptanoate. CO<sub>2</sub> and CO were found in the analysis of the gas outlet stream.

The NiMo catalyst was selective for saturated hydrocarbons, and the CoMo catalyst for unsaturated hydrocarbons. The NiMo catalyst produced heptane with a selectivity of about 50% and the CoMo catalyst produced heptenes with a selectivity of about 40% as the main products (Fig. 5). On both catalysts, the major oxygen-containing compounds were heptanol and heptyl heptanoate, and their amounts were clearly higher on the CoMo catalyst than the NiMo catalyst (Fig. 5).

In the batch reactor, the acid conversion on the NiMo catalyst was complete after 45 min and total HDO was achieved after 1 h. Hydrocarbons and oxygen-containing compounds in the liquid samples were the same as in the flow reactor experiments. 1-Heptanethiol was the sulphur-containing compound found in the reaction mixture. In addition, CO, CO<sub>2</sub> and H<sub>2</sub>S were detected in the gas phase. The concentration profiles of the major products are depicted in Fig. 6. Hexenes and heptyl heptanoate after the complete acid conversion (45 min), and heptanol and heptenes after about 1 h were no longer found in the liquid samples. The concentrations of heptane and hexane in the reaction mixture increased with respect to time.

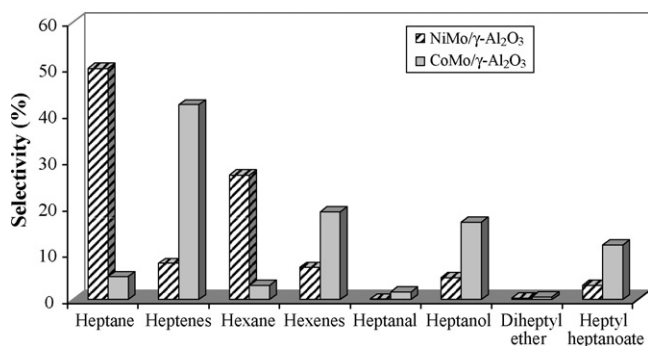


Fig. 5. Product distribution of heptanoic acid on sulphided NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and CoMo/γ-Al<sub>2</sub>O<sub>3</sub> catalysts at 250 °C under 1.5 MPa pressure in the flow reactor.

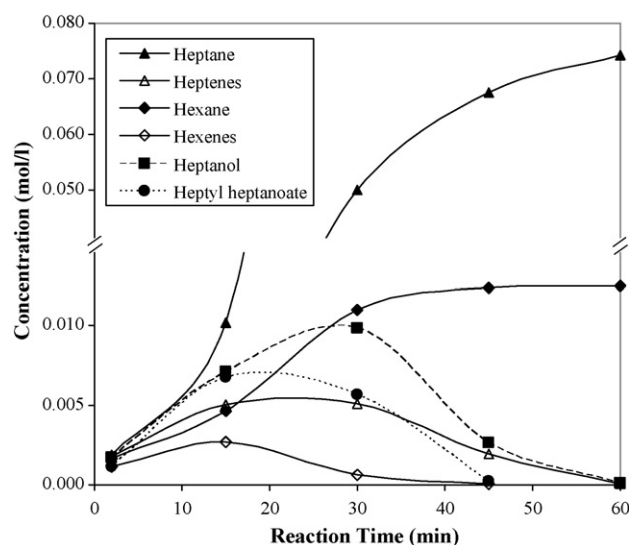


Fig. 6. Concentrations of products formed in the reactions of heptanoic acid on sulphided NiMo/γ-Al<sub>2</sub>O<sub>3</sub> catalyst at 250 °C under 7.5 MPa pressure in the batch reactor.

The sulphur and carbon contents of the catalysts changed in the reactions of heptanoic acid, as shown in Table 2.

## 4. Discussion

### 4.1. Reaction network

Presentation of the concentrations of the products as a function of time (Fig. 3) revealed, as we suggested previously [12], that heptanoic acid is a primary product formed in the reactions of methyl heptanoate. Heptanol did not accumulate in the reaction mixture indicating that it, too, was formed as an intermediate in the reactions. A carboxylic acid can be converted to an alcohol via an aldehyde. Thus, heptanol might have been formed by the hydrogenation of heptanal, which was detected in only trace amounts presumably due to its high reactivity. Since C<sub>6</sub> hydrocarbons were not formed in the reactions of heptanol, their formation may be explained in terms of reactions of heptanoic acid and heptanal. In a study of deoxygenation of stearic acid on various supported metal catalysts, Snåre et al. [14] found that saturated and unsaturated hydrocarbons were produced by decarboxylation and decarbonylation reactions, respectively. CO<sub>2</sub> and CO were formed as the side products. Similarly, heptanoic acid might produce saturated and unsaturated C<sub>6</sub> hydrocarbons on the sulphided NiMo and CoMo catalysts. Moreover, cleavage of CO from heptanal might yield C<sub>6</sub> hydrocarbons. Thus, carbon oxides might be produced in reactions of the ester and acid, which, as revealed by the thermodynamic data estimated with the HSC Chemistry<sup>®</sup> program [15] (Table 3), are not equilibrium-limited in gas phase at 250 °C.

The formation of heptanol and methanol in reactions of the ester in the absence of a catalyst clearly shows that heptanol was also produced directly from the ester even though the conversions were low.

Looking at Fig. 4, extrapolation of space time towards the y-axis can provide information about intermediates in the reactions

Table 3  
Thermodynamic data for possible reactions of heptanoic acid and heptanal in gas phase at 250 °C

|   | $\Delta G_{250}$ (kJ/mol) | $\Delta H_{250}$ (kJ/mol) |
|---|---------------------------|---------------------------|
| $C_6H_{13}COOH(g) \rightarrow C_6H_{14}(g) + CO_2(g)$             | -713                      | 17                        |
| $C_6H_{13}COOH(g) \rightarrow C_6H_{12}(g) + CO(g) + H_2O(g)$     | -635 <sup>a</sup>         | 185 <sup>b</sup>          |
| $C_6H_{13}COOH(g) + H_2(g) \rightarrow C_6H_{13}CHO(g) + H_2O(g)$ | -624                      | 74                        |
| $C_6H_{13}COOH(g) + 2H_2(g) \rightarrow C_7H_{15}OH(g) + H_2O(g)$ | -633                      | 15                        |
| $C_6H_{13}CHO(g) \rightarrow C_6H_{14}(g) + CO(g)$                | -72                       | -7                        |
| $C_6H_{13}CHO(g) \rightarrow C_6H_{12}(g) + CO(g) + H_2(g)$       | -13 <sup>a</sup>          | 121 <sup>b</sup>          |
| $C_6H_{13}CHO(g) + H_2(g) \rightarrow C_7H_{15}OH(g)$             | -9                        | -60                       |

<sup>a</sup> Gibb's free energy of formation of 1-hexene.

<sup>b</sup> Heat of formation of 1-hexene.

of heptanol. Thus, selectivities to heptenes and diheptyl ether approached 'non-zero' values with decreasing space time, while selectivity to heptane approximated to 'zero' value. Clearly, heptenes and diheptyl ether were formed as intermediates and heptane as the end product.

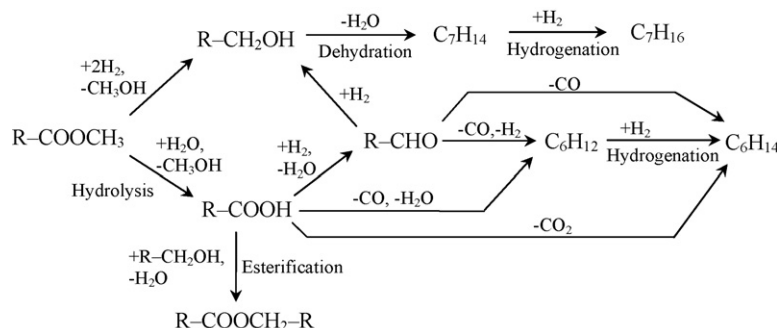
On the basis of these findings, we propose the reaction network of Scheme 1 for the HDO of methyl heptanoate. Previously, we reported the formation of  $C_6$  hydrocarbons directly from methyl heptanoate by means of decarboxylation reaction [12,13]. However, no direct evidence of this reaction was found in the present study and it is excluded from the reaction network. Note that the presence of carbon oxides, hydrogen and water in the reactor may lead to a number of reactions such as methanation and water-gas shift reactions. The formation of methane, for instance, might be explained in terms of methanation reactions. However, these reactions were not investigated in the present work.

#### 4.2. Reaction mechanisms

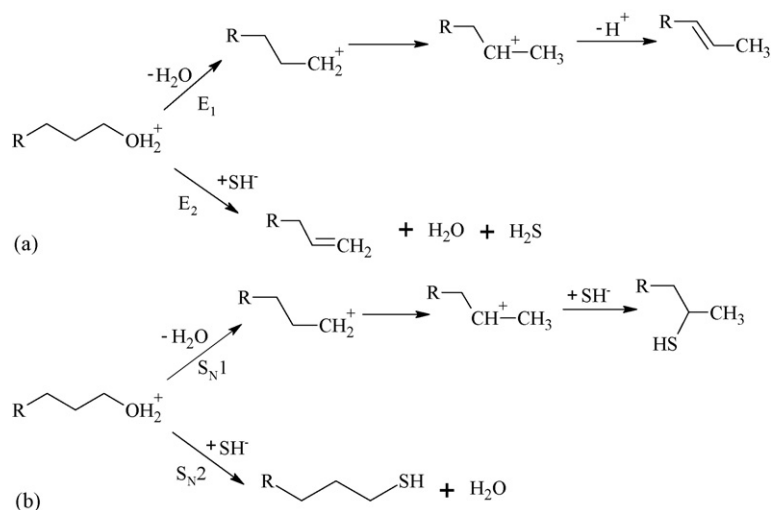
Esters can be converted to carboxylic acids by means of hydrolysis, which is the reverse of the acid-catalysed esterification reaction by which a carboxylic acid and an alcohol form an ester and water [22]. In addition, acid–base reactions are known to take place at high temperature on sulphided hydrotreating catalysts [17–22]. Correspondingly, heptanoic acid might be formed by the acid-catalysed hydrolysis of methyl heptanoate on the sulphided NiMo and CoMo catalysts. The reverse of the hydrolysis, i.e. esterification, might explain the formation of heptyl heptanoate from heptanol and heptanoic acid.

Water is needed for the hydrolysis reaction. Yet, the reactants were confirmed by NMR analysis to be water-free, and the calcination step at high temperature under nitrogen flow during the catalyst pretreatment should remove any water remaining in the pores. We assume, therefore, that water was not present at the beginning of the reactions under our experimental conditions. The formation of heptanoic acid in the absence of a catalyst in the batch reactor revealed that the acid was produced from the ester even though the conversion was low. According to Scheme 1, the acid was consumed in the reactions forming heptanal and heptyl heptanoate, which produce water as a side product. Similarly, heptanol generated directly from the methyl ester yielded heptenes by means of elimination of water. Thus, all these reactions increased the amount of water available for use in the hydrolysis reaction. In addition to this, the alumina support was earlier [12] found to catalyse the formation of carboxylic acids and alcohols from aliphatic methyl esters, but no hydrocarbons were formed. It is therefore not excluded that the alumina support, with its Lewis acid sites, might participate in the hydrolysis of the ester.

Alcohols can yield unsaturated hydrocarbons by means of acid-catalysed dehydration reaction, which, in principle, takes place by the  $E_1$  and  $E_2$  elimination mechanisms [16,23,24]. The formation of heptenes from heptanol by the elimination mechanisms is shown in Scheme 2a. According to the  $E_1$  mechanism, the split of water from protonated heptanol forms a primary carbenium ion, which is energetically unstable. Since the acidity of the sulphided catalysts is not sufficient to produce a primary carbenium ion [21], the  $E_1$  mechanism is very unlikely. Consequently, we propose that the formation of 1-heptene by the  $E_2$  mechanism, as seen in Scheme 2, was followed by acid-catalysed



Scheme 1. Reactions of methyl heptanoate on sulphided NiMo/ $\gamma$ - $Al_2O_3$  and CoMo/ $\gamma$ - $Al_2O_3$  catalysts ( $R=C_6H_{13}$ ).



Scheme 2. Acid-catalysed (a) elimination and (b) nucleophilic substitution mechanisms of 1-heptanol ( $R=C_4H_9$ ).

isomerisation to *cis/trans*-2-heptene and *cis/trans*-3-heptene to yield more stable internal heptenes [24]. In our previous study [12], HDO was found not to occur on the alumina support. Hence, coordinatively unsaturated sites (CUS), i.e. sulphur anion vacancies, on the sulphided catalysts are likely the active sites for the dehydration reaction.

Although elimination mechanisms are proposed to be responsible for the formation of heptenes from heptanol, they do not explain the formation of diheptyl ether and sulphur-containing compounds in the reactions. These compounds can be formed by the  $S_N1$  and  $S_N2$  nucleophilic substitution mechanisms. As illustrated in Scheme 2b, the  $S_N1$  mechanism produces 2-heptanethiol and the  $S_N2$  mechanism 1-heptanethiol. Since the  $S_N1$  mechanism leads to an unstable primary carbenium ion (Scheme 2b) and 2-heptanethiol was not detected among the products, the  $S_N1$  mechanism was concluded not to occur. The formation of 1-heptanethiol by the  $S_N2$  mechanism was likely followed by the elimination of  $H_2S$  and the formation of 1-heptene. If the nucleophile in the  $S_N2$  mechanism is another 1-heptanethiol molecule, the products are then diheptyl sulphide and  $H_2S$ , both of which were detected in the experiments. Similarly, the formation of diheptyl ether suggests that another heptanol molecule might act as a nucleophile, producing diheptyl ether and water from 1-heptanol. The formation of hexanethiol in the reactions of heptanoic acid suggests a possible role for the nucleophilic substitution reaction in the formation of  $C_6$  hydrocarbons as well. Indeed, the  $\alpha$ -carbon is more electrophilic in heptanoic acid and heptanal than in 1-heptanol owing to the presence of  $C=O$   $\pi$ -bond. As a result, heptanoic acid and heptanal are more susceptible to nucleophilic attack than 1-heptanol. Since no sulphiding agent was added during the reactions, the nucleophile needed for the formation of sulphur-containing compounds in the nucleophilic substitution mechanism was likely provided by reactive sulphur species, i.e. weakly bonded sulphur, on the sulphided catalysts. This also can explain the decreases in the sulphur contents. The formation of sulphur-containing compounds as intermediates supports the recent work of Prins et al. [18–22], which showed the for-

mation of sulphur-containing compounds as intermediates in acid-catalysed reactions on sulphided catalysts.

The formation of heptane may be explained in terms of two reactions: hydrogenation of heptenes and direct hydrogenolysis of 1-heptanol, which means cleavage of the C–O bond and simultaneous hydrogenation. In the reactions of heptanol under the same experimental conditions (Al-3 and Al-7), the NiMo catalyst, in accordance with its high hydrogenation activity [25], was selective to saturated hydrocarbon and the CoMo catalyst to unsaturated hydrocarbons (Table 1). On the basis of these observations, we conclude that the hydrogenation of heptenes is the major route to heptane, and the direct hydrogenolysis of 1-heptanol does not proceed at a discernible rate under the studied conditions.

#### 4.3. Catalyst activities

The rapid decreases in the conversion levels of the methyl ester and acid at the beginning of the reactions in the flow reactor revealed an initial deactivation of the catalysts. Increasing carbon contents and decreasing sulphur contents during the reactions indicated coke formation and desulphurisation of the catalysts, which led to the deactivation [26].

In the reactions of the ester and acid in the flow reactor, total conversion and HDO conversion were always higher on the NiMo catalyst than on the CoMo catalyst, which suggests that the NiMo catalyst is more favourable for the HDO of aliphatic oxygen-containing compounds such as esters, alcohols and carboxylic acids. Unfortunately, hydrogen consumption is increased with the NiMo catalyst.

## 5. Conclusions

Reactions of aliphatic methyl esters on sulphided NiMo/ $\gamma$ - $Al_2O_3$  and CoMo/ $\gamma$ - $Al_2O_3$  catalysts were investigated in flow and batch reactors with methyl heptanoate, heptanol and heptanoic acid as reactants. Methyl heptanoate produced saturated and unsaturated  $C_7$  and  $C_6$  hydrocarbons in a complex reaction

network in which oxygen-containing and sulphur-containing compounds were formed as intermediates. Sulphur-containing compounds led to desulphurisation of the catalysts. Heptanol and heptanoic acid were the primary products of the methyl ester. Heptanol yielded C<sub>7</sub> hydrocarbons and heptanoic acid C<sub>7</sub> and C<sub>6</sub> hydrocarbons. Heptane on the NiMo catalyst and heptenes on the CoMo catalyst were the main products. The reactions of aliphatic ester, alcohol and acid on sulphided catalysts were explained in terms of hydrogenation reactions and acid-catalysed reactions such as hydrolysis, dehydration and esterification. The NiMo catalyst exhibited better activity for the conversion of aliphatic oxygen-containing compounds than the CoMo catalyst, but it consumed more hydrogen.

## References

- [1] D. Mohan, C.U. Pittman Jr., P.H. Steele, *Energy Fuels* 20 (2006) 848–889.
- [2] S. Czernik, A.V. Bridgwater, *Energy Fuels* 18 (2004) 590–598.
- [3] R.K. Sharma, N.N. Bakhshi, *Can. J. Chem. Eng.* 69 (1991) 1071–1081.
- [4] A.V. Bridgwater, *Appl. Catal. A: Gen.* 116 (1994) 5–47.
- [5] E. Furimsky, *Appl. Catal. A: Gen.* 199 (2000) 147–190.
- [6] E. Laurent, B. Delmon, *Appl. Catal. A: Gen.* 109 (1994) 77–96.
- [7] E. Laurent, B. Delmon, *Appl. Catal. A: Gen.* 109 (1994) 97–115.
- [8] A. Centano, E. Laurent, B. Delmon, *J. Catal.* 154 (1995) 288–298.
- [9] M. Ferrari, S. Bosmans, R. Maggi, B. Delmon, P. Grange, *Catal. Today* 65 (2001) 257–264.
- [10] M. Ferrari, R. Maggi, B. Delmon, P. Grange, *J. Catal.* 198 (2001) 47–55.
- [11] M. Ferrari, B. Delmon, P. Grange, *Microporous Mesoporous Mater.* 56 (2002) 279–290.
- [12] O.İ. Şenol, T.-R. Viljava, A.O.I. Krause, *Catal. Today* 100 (2005) 331–335.
- [13] O.İ. Şenol, T.-R. Viljava, A.O.I. Krause, *Catal. Today* 106 (2005) 186–189.
- [14] M. Snåre, I. Kubičková, P. Mäki-Arvela, K. Eränen, D.Y. Murzin, *Ind. Eng. Chem. Res.* 45 (2006) 5708–5715.
- [15] A. Roine, *Outokumpu HSC Chemistry® User's Guide, Version 5.1*, Outokumpu Research Oy, Pori, Finland, 2002.
- [16] F.A. Carey, *Organic Chemistry*, fourth ed., McGraw-Hill, 2000.
- [17] N.-Y. Topsøe, H. Topsøe, *J. Catal.* 139 (1993) 641.
- [18] R. Prins, Y. Zhao, N. Sivasankar, P. Kukula, *J. Catal.* 234 (2005) 509–512.
- [19] R. Prins, M. Egorova, A. Röthlisberger, Y. Zhao, N. Sivasankar, P. Kukula, *Catal. Today* 111 (2006) 84–93.
- [20] Y. Zhao, R. Prins, *J. Catal.* 229 (2005) 213–226.
- [21] Y. Zhao, R. Prins, *J. Catal.* 222 (2004) 532–544.
- [22] F. Rota, R. Prins, *J. Mol. Catal. A: Chem.* 162 (2000) 367–374.
- [23] A. Streitwieser, C.H. Heathcock, E.M. Kosower, *Introduction to Organic Chemistry*, fourth ed., MacMillan Publishing Company, New York, 1992.
- [24] R.J. Fessenden, J.S. Fessenden, *Organic Chemistry*, third ed., Brooks/Cole Publishing Co., California, 1982.
- [25] H. Topsøe, B.S. Clausen, F.E. Massoth, *Hydrotreating Catalysts: Science and Technology*, Springer, Germany, 1996.
- [26] E. Furimsky, F.E. Massoth, *Catal. Today* 52 (1999) 381–495.