

# From Sulfided to Noble Metal Catalysts in the Hydrodeoxygenation of Aliphatic Esters

Andrea Gutierrez\*, Maija Honkela, Eeva-Maija Ryymin, and Outi Krause  
Helsinki University of Technology, Faculty of Chemistry and Materials Sciences,  
Kemistintie 1, 02150 Espoo (Finland)  
\*andrea.gutierrez@tkk.fi

## Introduction

Hydrodeoxygenation (HDO), i.e. the removal of oxygen in the presence of hydrogen, is conventionally carried out on sulfided alumina-supported CoMo and NiMo catalysts. During the operation, sulfiding agents have to be added to avoid sulfur leaching from the surface thus maintaining the activity of the catalysts [1,2]. ZrO<sub>2</sub>-supported noble metal (Rh, Pt, and Pd) catalysts offer a new possibility to carry out HDO in the absence of sulfur: they have been found to be active and selective in the HDO of 2-methoxyphenol (guaiacol, GUA) [3], used as a model component for wood-based pyrolysis oil. Higher selectivity to benzene and lower carbon deposition were obtained with the noble metal than with the sulfided catalyst at 300 °C. Due to these promising results it is of interest to test the noble metal catalysts in the HDO of methyl heptanoate, which can be used as a model component for vegetable oils. The reaction scheme on the sulfided catalysts is presented in Figure 1. Heptanal and heptanol were identified as important reaction intermediates [2]. The main product is heptane and also hexane is produced through decarbonylation reactions.

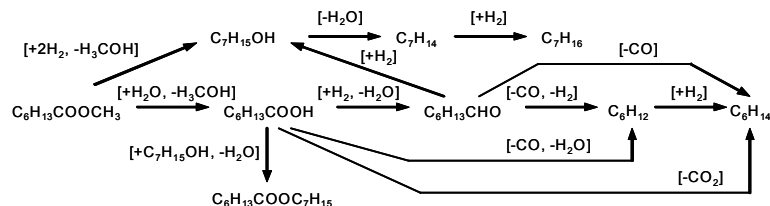


Figure 1. Reaction network of methyl heptanoate with sulfided catalysts [2].

The best performing catalyst in the HDO of GUA was Rh/ZrO<sub>2</sub> [3]. The aim of this work was to study the applicability of the Rh/ZrO<sub>2</sub> catalyst in the HDO of methyl heptanoate and to derive further knowledge about the reaction pathways on the noble metal catalyst.

## Materials and Methods

The experiments were performed in a 40 ml stainless steel batch reactor at 250 °C and 8 MPa. Drying in air and reduction of the 0.5 wt% Rh/ZrO<sub>2</sub> catalyst were performed in situ at 1 MPa and 400 °C for 1 h each. After the pretreatment a 5 wt% solution of methyl heptanoate, heptanol or heptanal in solvent (dodecane) was charged to the reactor and the pressure was increased with H<sub>2</sub>. Liquid and gas samples were analyzed with GC-MS and GC, respectively. For comparative purposes, experiments with sulfided Al<sub>2</sub>O<sub>3</sub>-supported NiMo catalysts (5 vol% H<sub>2</sub>S in H<sub>2</sub> for 2 h) were performed in another batch reactor.

## Results and Discussion

The conversion of methyl heptanoate with the Rh/ZrO<sub>2</sub> catalyst was 30% after 90 min. Heptanoic acid and hexane were the main products (Table 1). The experiments performed with heptanol and heptanal as reactants gave 20% and 100% conversion after 90 min, respectively. Hexane (95 mol%) was the main product from heptanol. Hexane (10 mol%) and heptanol (90 mol%) were obtained as products from heptanal. Independent of the reactant, the gas phase was composed of unreacted H<sub>2</sub> and CH<sub>4</sub>.

In Table 1 the product distribution with the ester with the Rh/ZrO<sub>2</sub> and with the sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> are compared. The comparison is made at conversion level of 30-40%. The selectivity towards hexane was significantly higher with the noble metal than with the sulfided catalyst, while the reaction pathway to heptane, highly active with the sulfided catalyst, was now suppressed. Also the side reaction to heptyl heptanoate was somewhat hindered.

Table 1. Product distribution (mol%) in the liquid phase with Rh/ZrO<sub>2</sub> and sulfided NiMo/Al<sub>2</sub>O<sub>3</sub>. Unreacted methyl heptanoate is included.

Compound	Rh	NiMo	Compound	Rh	NiMo
methanol H <sub>3</sub> COH	1	2	methyl heptanoate C <sub>6</sub> H <sub>13</sub> COOCH <sub>3</sub>	72	68
hexane C <sub>6</sub> H <sub>14</sub>	9	3	heptanoic acid C <sub>6</sub> H <sub>13</sub> COOH	14	7
heptane C <sub>7</sub> H <sub>16</sub>	0.1	6	heptyl heptanoate C <sub>6</sub> H <sub>13</sub> COOC <sub>7</sub> H <sub>15</sub>	2	7
hexenes C <sub>6</sub> H <sub>12</sub>	0	1	heptanal C <sub>6</sub> H <sub>13</sub> CHO	0.1	0.5
heptenes C <sub>7</sub> H <sub>14</sub>	0	2	heptanol C <sub>7</sub> H <sub>15</sub> OH	2	3

The dehydration of heptanol to heptene is suppressed with the Rh/ZrO<sub>2</sub> catalyst based on the results obtained with heptanol. The main reaction of heptanol is the reaction to hexane. It is probable that from the ester hexane is not significantly produced through heptanal, because heptanal reacts easily to heptanol the amount of which, however, remained small. Furthermore, the reactivity of heptanol to hexane is low as demonstrated by our experiments. Thus heptanol and heptanal seem not to be important intermediates in the HDO of methyl heptanoate on the noble metal catalyst. Instead, one possible pathway to hexane is the decarboxylation of heptanoic acid formed in the first step, giving CO<sub>2</sub> as a side product. CO<sub>2</sub> reacts further with H<sub>2</sub> to form CH<sub>4</sub>, the main product of the gas phase. The high activity for hydrogenation reactions is typical for noble metal catalysts. With the sulfided catalyst small amounts of alkenes and CO were detected suggesting that the sulfided catalysts are not as active as the noble metal catalysts in hydrogenation.

## Significance

The Rh/ZrO<sub>2</sub> catalyst is active in the HDO of methyl heptanoate producing selectively hexane. Based on the results, this type of noble metal catalysts could be used in the HDO of aliphatic esters.

## References

- A.V. Bridgwater, *Catal. Today*, 29, 285, (1996).
- O.İ. Şenol, T.-R. Viljava, A.O.I. Krause, *Appl. Catal. A*, 326, 236, (2007).
- A. Gutierrez, R.K. Kaila, M.L. Honkela, R. Slioor, A.O.I. Krause, *Catal. Today*, (2008), accepted for publication.