Journal of Catalysis 328 (2015) 197-207

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

# Selective hydrogenation of fatty acids to alcohols over highly dispersed $ReO_x/TiO_2$ catalyst



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# ARTICLE INFO

Article history: Received 8 August 2014 Revised 5 November 2014 Accepted 3 January 2015

The paper is dedicated to the living memory of Dr. Haldor Topsøe.

Keywords: Fatty acids Fatty alcohols Rhenium Selective hydrogenation Hydrocarbons

## 1. Introduction

Fatty alcohols are non-ionic surfactants widely used as emulsifiers, emollients and thickeners in alimentary and cosmetic industries [1]. Moreover, they can be substrates for the production of other surface-active materials, such as alkylamines and alkylsulfates. The current world production capacity of fatty alcohols reaches 3.35 Mt/a, with an estimated global demand growth (2012–2017) of 3.2%/a [2]. Fatty alcohols are mainly produced through catalytic hydrogenation of fatty acids, methyl esters or wax esters. In traditional processes, the methyl esters are hydrogenated over Cu–Cr-based [3] catalysts with a high selectivity towards alcohols. However, due to low reactivity of the carboxyl group, elevated temperatures (200–300 °C) and hydrogen pressures (20–30 MPa) have to be applied. Moreover, chromium catalysts are not environmentally friendly due to a release of hazardous chromium compounds.

Noble metal catalysts such as Ru or Pt were reported to be active in selective hydrogenation of fatty acids. Many kinds of Ru-based catalysts have been studied [4], from which bimetallic

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# ABSTRACT

Production of fatty alcohols through selective hydrogenation of fatty acids was studied over a 4%  $\text{ReO}_{x/}$ TiO<sub>2</sub> catalyst. Stearic acid was hydrogenated to octadecanol at temperatures and pressures between 180–200 °C and 2–4 MPa, with selectivity reaching 93%. A high yield of octadecanol was attributed to a strong adsorption of the acid compared to alcohol on the catalyst, which inhibits further alcohol transformation to alkanes. Low amounts (<7%) of alkanes (mainly octadecane) were formed during the conversion of stearic acid. However, it was found that the catalyst could be tuned for the production of alkanes. The reaction intermediates were octadecanal and stearyl stearate. Based on the reaction products analysis and catalyst characterization, a reaction mechanism and possible pathways were proposed.

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Ru–Sn/Al<sub>2</sub>O<sub>3</sub> [5] shows the highest selectivity towards fatty alcohols (250 °C; 5.6 MPa) in methyl laurate hydrogenation. In addition, a change of the support in the Ru–Sn catalyst from Al<sub>2</sub>O<sub>3</sub> to TiO<sub>2</sub> increases the activity and selectivity which is ascribed to Ru–Ti metal–support interactions [6]. The same properties were observed with a Pt/TiO<sub>2</sub> catalyst [7] as hydrogenation of fatty acids to alcohols was performed at relatively low temperatures (110–150 °C) and hydrogen pressures (2 MPa) with selectivity 90–93%. It is assumed that an enhanced activity is caused by the Ti<sup>3+</sup> ion/oxygen vacancy on the metal–support interface, which interacts with the carbonyl oxygen and weakens C=O bond, promoting hydrogenation of the carboxylic acid [6,7].

Rhenium catalysts were disclosed in the patent literature as being capable of hydrogenating carbonyl compounds to alcohols with high overall selectivity, without formation of ethers. Selective hydrogenation of fatty acids to alcohols was also studied over rhenium-based catalysts. Decanoic acid transformation has been performed over  $\text{Re}_2\text{O}_7$  at 10 MPa of hydrogen and 130 °C, giving a low conversion and a moderate selectivity towards 1-decanol [8]. Moreover, it has been shown that an addition of OsO<sub>4</sub> to form a bimetallic Re–Os [8] catalyst increases not only the rate but also the selectivity to 84%. Furthermore, Re and bimetallic Re–Sn deposited over ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have been studied at 250 °C and





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5.6 MPa of hydrogen pressure in the hydrogenation of oleic acid. The Re/Al<sub>2</sub>O<sub>3</sub> catalyst afforded the highest selectivity to alcohols, reaching 58% [9].

In this work,  $Re/TiO_2$  was studied in the selective hydrogenation of stearic acid to 1-octadecanol, displaying high selectivity of 93% under mild reaction conditions. Unusual properties of Re allow a selective conversion of fatty acids suppressing the formation of by-products. Moreover, the catalyst can be tuned for the production of hydrocarbons.

## 2. Experimental

## 2.1. Catalyst preparation

Titania P-90 and perrhenic acid (assay 39.4%) were supplied by Nippon Aerosil and Johnson Matthey, respectively. The Re catalysts were prepared by incipient wetness impregnation. An appropriate mass of the perrhenic acid solution was diluted with deionised water ( $18 M\Omega$ ) of volume equal to the pore volume of the support. The solution was added to the support in three portions of equal volumes with stirring after each addition, until the solution was thoroughly mixed. The product was then dried at 120 °C for 12 h, followed by calcination at 500 °C for 4 h.

#### 2.2. Temperature-programmed reduction (TPR)

Prior to the analysis, 50 mg of non-reduced Re/TiO<sub>2</sub> catalyst was kept in an oven at 100 °C overnight. Temperature-programmed reduction was performed in an Autochem Micromeritics 2910 using 5% H<sub>2</sub> in Ar. The temperature ramp was 10 °C/min to 500 °C.

### 2.3. Temperature-programmed desorption (TPD)

Temperature-programmed desorption was performed in an Autochem Micromeritics 2910. Ammonia and carbon dioxide were used for the determination of the acid and base sites, respectively. The sample was at first kept under a helium atmosphere at 400 °C for 1 h then cooled to 100 °C, in the case of NH<sub>3</sub> TPD, and 30 °C, in the case of CO<sub>2</sub> TPD. Afterwards, the adsorbate was introduced for 30 min. Subsequently, the catalyst was flushed with an inert gas for 30 min after which the analysis was started. The temperature ramp was 10 °C/min up to 700 °C for NH<sub>3</sub> and 600 °C for CO<sub>2</sub> where the sample was kept for 1 h. Before the adsorption, the Re/TiO<sub>2</sub> catalyst was reduced *in situ* with hydrogen at 400 °C for 2 h.

#### 2.4. CO chemisorption

CO chemisorption was performed in an Autochem Micromeritics 2910. The Re/TiO<sub>2</sub> catalyst was reduced *in situ* with hydrogen prior to the analysis at 400 °C for 2 h. The hydrogen excess was removed by flushing the catalyst with helium at reduction temperature for 30 min. Pulse chemisorption was performed in a quartz glass reactor performed at 25 °C and glass reactor submerged in a water bath for temperature control.

### 2.5. Transmission electron microscopy (TEM)

The rhenium particle-size distribution was measured by a JEM-1400 Plus Transmission Electron Microscope (voltage 120 kV). The sample was reduced at 400  $^{\circ}$ C for 2 h before analysis. Histograms of the particle-size distribution were obtained by counting at least 100 particles on the micrographs for the sample.

## 2.6. Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP– OES)

The Re content of the catalyst was determined by Inductively Coupled Plasma (ICP) using an Optical Atomic-Emission Spectrometer Optima 4300 DV. For the analysis of the Re content, the Re/TiO<sub>2</sub> catalyst was dissolved in a microwave oven by an acid mixture (2 ml  $H_2SO_4 - 96\% + 2$  ml  $H_3PO_4 - 85\% + 1$  ml HF - 40% + 0.5 ml HNO<sub>3</sub> - 65%).

## 2.7. Nitrogen physisorption

The specific surface area of the fresh catalyst was measured by nitrogen physisorption using a Sorptometer 1900 (Carlo Erba instruments) apparatus. Prior to the analysis, the sample was degassed at 200 °C for 3 h. The specific surface area was calculated by BET equation.

## 2.8. X-ray photoelectron spectroscopy (XPS)

The Re/TiO<sub>2</sub> catalyst was reduced at atmospheric pressure and at 0.5 MPa in hydrogen. The catalyst was transported under acetone to a glove box where it was filtered and dried at room temperature in an inert atmosphere. The spent catalyst was transported after the reaction to the glove box submerged in reaction mixture. At inert atmosphere, the catalyst was washed with acetone and dried at room temperature. All catalysts were brought to the XPS equipment in sealed containers. During the insertion to the XPS equipment, the catalyst had less than 2-min contact with air.

A Perkin–Elmer PHI 5400 spectrometer with a Mg K $\alpha$  X-ray source operated at 14 kV and 200 W was used in the XPS analysis of the samples. The pass energy of the analyser was 17.9 eV and the energy step 0.05 eV. The binding energy calibration was based on the Ti  $2p_{3/2}$  peak at 458.8 eV. Fitting of the XPS data was performed after removal of Shirley background using Voigt profile. In the peak fitting procedure, the Re  $4f_{5/2}$  and Re  $4f_{7/2}$  intensity ratio was 0.75 and energy separation was 2.43 eV. The sensitivity factors used in the quantitative analysis for O 1s, Ti  $2p_{3/2}$ , Re 4f and C 1s were 0.711, 1.334, 3.961 and 0.296, respectively.

## 2.9. Kinetic experiments

In all of the kinetic experiments, the reaction mixture was prepared from 1 g (0.0035 mol) of stearic acid (Merck 97%) and dissolved in 100 ml of dodecane (Sigma–Aldrich 99%) at 60 °C. The solution was injected to a heated pre-reactor at 90 °C. To remove air, the pre-reactor was flushed with inert gas, which afterwards was substituted with hydrogen.

Experiments were performed in a high-pressure steel Parr reactor at temperature range 180–220 °C and total over pressure was 2–4 MPa in hydrogen (AGA, 5.0). The catalyst (0.1 g) was reduced *ex situ*, under a hydrogen atmosphere (1 bar) for 2 h at 400 °C (temperature was selected based on Re/TiO<sub>2</sub> TPR – Fig. 2) with a heating ramp of 2 °C/min. After the reduction, the catalyst was immediately transferred to the reactor. The air in the reactor was substituted first with inert gas and subsequently with 0.2 MPa of hydrogen. Thereafter, the reactor was heated (5 °C/min) to the desired temperature at which the reaction mixture was injected together with hydrogen to achieve the desired pressure. The propeller stirrer with a stirring rate set to 1200 rpm was used to exclude external mass transfer limitations. The internal mass transfer limitations can be excluded as a grain size of titania support was below 63 µm.

In the experiment with the non-reduced  $\text{Re}/\text{TiO}_2$ , the catalyst was placed in the reactor at room temperature and flushed with argon to remove air. Afterwards, temperature was raised to

220 °C. Reactants and hydrogen were injected at the same time and the stirring was started.

## 2.10. Product analysis

The analysis of the liquid phase was performed using gas chromatography (HP 5890) containing ZB-5 Inferno column (30 m, 0.32 mm, 0.1  $\mu$ m). Samples for analysis were prepared by mixing 0.1 ml of the reaction mixture with 0.1 ml of the silylation agent (BSTFA, Sigma–Aldrich), 0.1 ml of eicosane (Acros Organics, 99%) dissolved in dodecane (1 mg/ml) as an internal standard and 1 ml of pyridine (Sigma–Aldrich, 99.9%). Thereafter, the samples were left in the oven at 70 °C for 1 h to ensure a proper silylation before injection to the GC. The same sample preparation procedure was performed before the qualitative analysis in GC–MS (GC-6890N, MS-5973) with the chromatographic column DB-PETRO (100 m, 0.25 mm, 0.5  $\mu$ m).

# 3. Results and discussion

#### 3.1. Catalyst characterization

Temperature-programmed desorption (TPD) of NH<sub>3</sub> and CO<sub>2</sub> was used to determine the strength and the amount of acid and basic sites. The NH<sub>3</sub> TPD of non-impregnated TiO<sub>2</sub> shows weak acid sites with a desorption maximum at 140 °C. The Re/TiO<sub>2</sub> catalyst showed two maxima at 198 °C and 368 °C, indicating two kinds of acid sites (Fig. 1a). The total volume of ammonia adsorbed over the Re/TiO<sub>2</sub> catalyst was 18 times higher than of bare TiO<sub>2</sub>, indicating a high increase of the acidity after the deposition of rhenium (Table 1). However, it has to be pointed out that the decomposition of ammonia over rhenium can occur at temperatures around 350 °C, which could influence the generation of the second peak [10].

The TPD of CO<sub>2</sub> was performed similar to that of NH<sub>3</sub> on TiO<sub>2</sub> and Re/TiO<sub>2</sub> catalysts. Pure TiO<sub>2</sub> showed a desorption peak at a low temperature (92 °C), while after the deposition of rhenium,



**Fig. 1.** (a)  $NH_3$ -TPD and (b)  $CO_2$ -TPD of (red)  $Re/TiO_2$  and (black)  $TiO_2$ . (For the interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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Properties of 4%	ReO <sub>x</sub> /TiO <sub>2</sub> catalyst.
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	Surface area (m²/g)	Pore volume (ml/g)	Basicity (µmol/g)	Acidity (µmol/g)	Average particle size (nm)	Metal loading (wt.%)
TiO <sub>2</sub>	108	0.18	37	15	-	-
Re/TiO <sub>2</sub>	63	0.22	531	270	0.9 ± 0.03	3.8

three kinds of sites were found with maxima at 80 °C, 161 °C and 348 °C (Fig. 1b), with total volume of  $CO_2$  adsorbed increasing over 14 times (Table 1).

#### 3.1.1. Oxidation state of rhenium

The TPR analysis shows that the reduction of rhenium starts at around 200 °C and passes through two maxima at 278 °C and 330 °C (Fig. 2). In all of the experiments, the catalyst was reduced at 400 °C for 2 h. At the same time, the XPS analysis revealed that the catalyst while being active was not fully reduced under these conditions (Fig. 3b) and contains  $\text{Re}^{7+}$ ,  $\text{Re}^{6+}$  and  $\text{Re}^{4+}$  species, which is in agreement with the previous studies on the reduction of supported rhenium [11].  $\text{Re}^{7+}$  was reduced during the reaction to form  $\text{Re}^{6+}$  and  $\text{Re}^{4+}$  (Fig. 3c). Moreover, similar catalyst oxidation states were found after the reaction independently on the reduction state of the catalyst before an experiment (Re-oxide/TiO<sub>2</sub> or reduced Re/ TiO<sub>2</sub>) (Table 2). Furthermore, there were no traces of metallic  $\text{Re}^{0}$ species in the fresh and spent catalysts suggesting that  $\text{ReO}_x$  is the active component in the selective hydrogenation of fatty acids to alcohols.

It is important to mention that rhenium has a high affinity to oxygen, which increases with the metal dispersion [12]. A highly dispersed catalyst, which is prepared in this work, can be oxidized upon contact with air. To confirm this hypothesis, the reduced sample was separated into two parts. The first part was kept under an inert atmosphere, while the second one was exposed to air at room temperature for 15 min. Thereafter, the catalysts were analysed with XPS. This experiment confirmed that even a short exposure to air at room temperature can result in the partial oxidation of  $\text{Re}^{6+}$  and/or  $\text{Re}^{4+}$  to  $\text{Re}^{7+}$  (Table 2).

### 3.1.2. Particle size of rhenium

The rhenium particle-size distribution were measured by transmission electron microscopy (TEM) technique, showing a very high dispersion of rhenium (close to 100%) with an average particle size calculated from the images being  $0.9 \pm 0.03$  nm (Fig. 4). For comparison, CO chemisorption on the catalyst was also performed



Fig. 2. Temperature-programmed reduction (TPR) of 4% ReO<sub>x</sub>/TiO<sub>2</sub> catalyst.



**Fig. 3.** XPS rhenium species for (a) non-reduced catalyst; (b) reduced catalyst at 400 °C for 2 h and (c) spent catalyst after reaction with pre-reduced catalyst.

 Table 2

 The area (%) for rhenium species in XPS analysis of 4% ReO<sub>3</sub>/TiO<sub>2</sub> catalyst.

4% ReO <sub>x</sub> /TiO <sub>2</sub>	Peak area (%)					
	Re <sup>4+</sup>	Re <sup>6+</sup>	Re <sup>7+</sup>			
Non-reduced <sup>a</sup>	0	31	69			
Pre-reduced <sup>b</sup>	47	36	17			
Spent (non-reduced) <sup>c</sup>	73	27	0			
Spent (pre-reduced) <sup>d</sup>	58	37	5			
Oxidized (pre-reduced) <sup>e</sup>	49	30	21			

<sup>a</sup> Fresh non-reduced catalyst.

<sup>b</sup> Fresh pre-reduced catalyst at 400 °C for 2 h in H<sub>2</sub> (0.1 MPa).

<sup>c</sup> Spent catalyst after reaction at 220 °C and 2 MPa of total pressure (without prereduction).

 $^d$  Spent catalyst after reaction at 220 °C and 2 MPa of total pressure (pre-reduced in  $H_2$  at 400 °C and 0.1 MPa for 2 h).

 $^e$  Fresh catalyst after pre-reduction at 400 °C for 2 h in H\_2 (0.1 MPa) and subsequent exposure on air at room temperature for 15 min.

and the calculated (with assumed stoichiometric factor CO/Re = 1) dispersion was 35%. The differences between TEM and CO chemisorption can be explained by the partial reduction of rhenium. Re<sup>4+</sup> and Re<sup>6+</sup> binds much weaker CO than Re<sup>0</sup> since rhenium cations have less electrons to back-donate to the CO ligand [13]. This results in a lower CO uptake and subsequently underestimation of the dispersion.

### 3.2. Hydrogenation of stearic acid

The hydrogenation of stearic acid over  $\text{ReO}_x/\text{TiO}_2$  was performed in the temperature range between 180 °C and 220 °C in hydrogen at a total pressure between 2 and 4 MPa. The main product was octadecanol (Fig. 5a). The experiments showed that the product formation can be achieved with a high activity even at temperatures below 200 °C. The initial activity of the catalyst (calculated at 30 min for each reaction) at 2 MPa total pressure varied from 0.07 (mol<sub>stearic acid</sub>  $g_{Re}^{-1}$  h<sup>-1</sup>) to 0.39 between 180 and 220 °C (Fig. 5b). Moreover, an increase in the hydrogen pressure enhances the reaction rate. It was observed that, at 200 °C, an increasing the hydrogen pressure from 2 to 3 to 4 MPa resulted in an increased conversion of 40% and 70% after 30 min reaction time, respectively. The apparent reaction order with respect to hydrogen was close to unity.

The formation of the alcohol from the acid over  $\text{ReO}_x/\text{TiO}_2$  catalyst occurs through an aldehyde intermediate, which is formed at the beginning of the reaction and passes through a maximum. Simultaneously, small amounts of hydrocarbons were observed. Octadecane and octadecene were formed by dehydration and subsequent hydrogenation (only octadecane) of octadecanol, while heptadecane and heptadecene were the products of stearic acid decarboxylation or octadecanal decarbonylation/dehydroformylation. Similar reaction pathways have been proposed for deoxygenation of fatty acid over noble-metal-supported catalysts at higher temperatures [14]. Furthermore, the formation of a wax ester (stearyl stearate) was observed, which appears after ~10% of stearic acid conversion from the reaction of stearic acid with 1-octadecanol. Based on the product distribution, the reaction pathway is proposed (Scheme 1).

The selectivity to octadecanol increases with the conversion of stearic acid reaching 88–93% at a high conversions (Fig. 6a and b). The aldehyde formation is prominent at low conversion levels, while ester formation influences the final selectivity at high conversion level. The formation of alkane is visible during the whole reaction. The selectivity to hydrocarbons is not strongly affected by a change of the reaction conditions, in contrary to the selectivity towards the aldehyde and the ester.

The initial selectivity towards the aldehyde can be as high as 45% for the reaction at 220 °C and 2 MPa of total pressure. However, a decrease of the temperature at 2 MPa of total pressure decreases the rate of aldehyde formation (Fig. 6c), therefore, increasing the initial selectivity to the alcohol. Moreover, it can be observed that the hydrogen pressure does not influence the selectivity towards the aldehyde (Fig. 6d). On the contrary, the formation of stearyl stearate at high conversion levels can be inhibited by a high hydrogen pressure that decreases the selectivity to ester from 3.5% to 1.5% (conversion = 80%) in experiments at 2 MPa and 4 MPa of total pressure, respectively. The decrease of temperature had no influence on the selectivity towards the ester.

The selectivity to hydrocarbons remains constant below 5% between 20% and 90% of the stearic acid conversion. During initial conversion period, an increased formation of alkanes can be observed (Fig. 7). Moreover, an increase of the hydrogen pressure does not influence the formation rates of the hydrocarbons as well as the distribution of hydrocarbon products. It was observed that lower reaction temperatures decrease the selectivity to total hydrocarbons. At 180 °C (2 MPa), no unsaturated products were found. Furthermore, the decarboxylation/decarbonylation rates decrease under these conditions, yielding less  $C_{17}$  hydrocarbons, while the rate of octadecanol hydrogenation to octadecane remains the same. In overall, the selectivity to 4%  $\text{ReO}_x/\text{TiO}_2$  at different temperatures and pressures can be seen in Table 3.

### 3.2.1. Formation of alkanes

During the conversion of stearic acid, the formation of hydrocarbons is minimal and stays at a level of around 4–5%. However, after a complete conversion of the acid, the rates of the alkane formation increase rapidly. For the experiment at 220 °C and 2 MPa of hydrogen pressure, the generation activity of the main hydrocarbon product (octadecane) increases from 0.01 (mol<sub>octadecane</sub>  $g_{Re}^{-1} h^{-1}$ ) – during the conversion of fatty acids (60–80%) – to 0.05 – during the later transformation of the alcohol (3–9%). This phenomenon can be



Fig. 4. (a) TEM image of pre-reduced at 400 °C for 2 h 4% ReO<sub>x</sub>/TiO<sub>2</sub> catalyst; (b) size distribution of rhenium nanoparticles over TiO<sub>2</sub>.



**Fig. 5.** (a) Reaction of stearic acid over 4%  $\text{ReO}_x/\text{TiO}_2$  catalyst at 220 °C in hydrogen at 2 MPa of total pressure; (b) activity of  $\text{Re}/\text{TiO}_2$  catalyst in stearic acid hydrogenation (mol<sub>stearic acid</sub>  $g_{\text{Re}}^{-1} h^{-1}$ ) calculated at t = 30 min.



Scheme 1. Reaction pathways of stearic acid conversion over 4% ReO<sub>x</sub>/TiO<sub>2</sub> catalyst.



Fig. 6. Selectivity (%) from conversion of stearic acid (%) over 4% ReO<sub>x</sub>/TiO<sub>2</sub> catalyst in hydrogen atmosphere to: (a) octadecanol and (c) octadecanal for reaction at 2 MPa of total pressure with temperatures between 180 and 220 °C; (b) octadecanol and (d) octadecanal at 200 °C with total pressure from 2 to 4 MPa.



**Fig. 7.** Selectivity to hydrocarbons (%) from conversion of stearic acid in hydrogen atmosphere over 4%  $\text{ReO}_x/\text{TiO}_2$  catalyst for reactions at temperature range between 180–220 °C and 2–4 MPa of total pressure.

caused by a difference of the adsorption strength between fatty acid and the alcohol. Since the acid is stronger adsorbed on the active site, the alcohol cannot adsorb and react to form alkanes. In the absence of stearic acid, the transformation of the alcohol takes place, and thus, competitive adsorption is the main reason of the unusually high selectivity of stearic acid conversion to octadecanol over  $\text{ReO}_x/\text{TiO}_2$  at medium temperatures and pressures.

As all acid was converted, the transformation of octadecanol took place. The main product of the octadecanol conversion is octadecane with a rising selectivity as the reaction proceeds (Fig. 8).

The ratio between the hydrogenation product (octadecane) and decarboxylation/decarbonylation product (heptadecane) increases with time as octadecanol is the main substrate for further transformation. However, a small amount of heptadecane was produced due to the conversion of stearyl stearate, which is still present in the system.

## 3.2.2. Reduction of the catalyst

A reaction with a non-reduced Re/TiO<sub>2</sub> catalyst was performed at 220 °C in 2 MPa H<sub>2</sub>. The conversion of stearic acids was significantly lower than in the reaction with the pre-reduced catalyst (Fig. 9a) with an initial activity of 0.06 (mol<sub>stearic</sub> acid  $g_{Re}^{-1} h^{-1}$ ) compared to 0.39 for pre-reduced catalyst at the same conditions. Moreover, the selectivity to the main product for the non-reduced catalyst is lower at all conversion levels, which is caused by an increased formation of hydrocarbons in comparison with the experiment with a pre-reduced catalyst (Fig. 9b).

The XPS measurements revealed that the oxidation state of rhenium for both non-reduced and pre-reduced spent catalysts was similar (Table 2), indicating that the reduction of rhenium for a non-reduced catalyst occurred during the reaction. However, a lower conversion in the experiment with the non-reduced catalyst indicates that the gas-phase pre-reduction step is crucial for the catalyst activity. It can be explained by a deficiency of the oxygen vacancies in titania, which formation requires a higher reduction temperature than used in the experiment [15]. During the prereduction of the catalyst at 400 °C, TiO<sub>2</sub> is partially reduced creating oxygen vacancies needed for the reaction to occur through the proposed mechanism, which is similar to the mechanisms suggested previously for the alcohol formation over titania-supported platinum [7] and ruthenium [6]. A shift in the binding energy of

Table 3Selectivity to products at different conversion levels in the reaction of stearic acid over  $4\% \text{ ReO}_x/\text{TiO}_2$  catalyst.

Temperature <i>T</i> Total pressure (°C) (MPa)	Selectivity at 20% conversion			Selectivity at 80% conversion			Selectivity to hydrocarbons at conversions	
	Octadecanol	Octadecanal	Stearyl stearate	Octadecanol	Octadecanal	Stearyl stearate	between 20% and 80%	
180	2	83	13	-	-	_	-	4
200	2	75	20	-	90	1.5	3.5	5
220	2	64	30	-	88	3.5	3.5	5
200	3	75	20	-	92	1.5	1.5	5
200	4	75	20	-	92	1.5	1.5	5



**Fig. 8.** Selectivity to  $C_{18}$  hydrocarbons from conversion of octadecanol in reaction of stearic acid over 4% ReO<sub>x</sub>/TiO<sub>2</sub> at 220 °C and 2 MPa of total pressure – after full stearic acid conversion.

rhenium species for the reduced catalyst can be ascribed to substantial interactions between rhenium and Ti<sup>3+</sup>. The Re–O–Ti<sup>3+</sup> sites are responsible for the formation of alcohol on which the carbonyl group of the acid is stronger adsorbed, thus inhibiting further transformations of the alcohol to hydrocarbons. A decrease in the titania oxygen vacancies on the interface with rhenium nanoparticles leads to a decrease of the number of sites on which adsorption of the acid is strong. Therefore, the alcohol can be more easily transformed to alkanes when the acid is still present in the system. This explains both lower conversion of fatty acids as a number of active sites for the reaction decreased and a higher formation of alkanes as the adsorption of alcohol on the catalyst increased. A similar effect was observed for hydrogenation of CO over  $\text{ReO}_x/\text{TiO}_2$  at 250 °C and 2.1 MPa [15].

## 3.3. Kinetic analysis

The reaction network for hydrogenation of stearic acid is displayed in Scheme 2. For the development of the kinetic model, it was assumed that all organic molecules are adsorbed on the same type of sites. The reaction order with respect to hydrogen is almost unity, which is consistent with low hydrogen coverage and its poor adsorption on rhenium compared to such metals as platinum. It was thus reasonable to assume that hydrogen from the fluid phase takes part in the reaction. Assumption of a pairwise addition of weakly adsorbed hydrogen would result in the same kinetic expression, while a concept of hydrogen adsorption with dissociation and stepwise addition of hydrogen atoms with the first step being the rate limiting in the spirit of the Horiuti-Polanyi mechanism inevitably results in the reaction order towards hydrogen equal to 0.5. Based on kinetic regularities, generation of an intermediate complex on the surface consisting of stearic acid and hydrogen can be considered as the rate-limiting step in the route from stearic acid to octadecanal while a further rearrangement of the surface complex to the aldehyde and water is fast. An analogous sequence of steps was supposed for hydrogenation of octadecanal to octadecanol. Transformations of the latter to a corresponding alkane require first dehydration to octadecene with subsequent hydrogenation.

Similar type of hydrogenation steps was considered in the literature [16]. Such sequence of steps can account for reaction orders in organic compounds ranging from zero to unity.

The reaction mechanism is comprised of four reaction routes (Schemes 2 and 3). In Schemes 2 and 3, SA is stearic acid, AD, AC,



Fig. 9. Comparison of reactions with pre-reduced and non-reduced catalysts at 220 °C and 2 MPa of total pressure: (a) conversion of stearic acid in time; (b) selectivity to octadecanol and hydrocarbons from conversion of stearic acid.



Scheme 2. Reaction network.

OE, OD and SS are, respectively, octadecanal, octadecanol, octadecene, octadecane and stearyl stearate. Sign \* in Scheme 2 denotes the active sites on the metal surface, while steps R1, etc. are reaction steps, while steps A1, etc. correspond to adsorption. The fast steps are denoted as, for example, R1'.

The schemes are based on the theory of complex reactions developed by Horiuti and extended by Temkin [17–19].

The elementary steps above can be described by four reaction routes, i.e. sets of stoichiometric numbers of steps. Elementary reactions are grouped in steps, and chemical equations of steps contain reactants and intermediate products. A set of stoichiometric numbers of steps is defined as a reaction route. Routes are essentially different, and it is impossible to obtain one route through multiplication of another route by a number, even in cases when their respective overall equations are identical. The number of basic routes, *P*, is determined by P = S + W - I, where *S* is the number of steps, *W* is the number of balance (link) equations and *I* is the number of intermediates. Such balance (link) equations can correspond to the total coverage of sites equal to unity. On the right hand side of equations for the steps, stoichiometric numbers

ble 4				
	-			

Parameter	Units	Value*	Relative standard error (%)
$k'_1$	bar <sup>-1</sup> min <sup>-1</sup>	$4.3\times 10^{-3}\pm 0.610^{-3}$	6.9
k' 2	bar <sup>-1</sup> min <sup>-1</sup>	$0.01 \pm 0.0026$	12.8
k' 3	min <sup>-1</sup>	$0.424  imes 10^{-3} \pm 0.17  10^{-3}$	20.1
$k'_4$	$(mol\%)^{-1} min^{-1}$	$0.382 \times 10^{-5} \pm 0.14  10^{-5}$	20.2
$E_1$	kJ/mol	106 ± 3	1.4
$E_2$	kJ/mol	39.3 ± 22	31.1
E <sub>3</sub>	kJ/mol	$70.6 \pm 40$	28.9
$E_4$	kJ/mol	86.3 ± 54	31.6
$K_1$	$(mol\%)^{-1}$	$0.025 \pm 0.004$	11.0

Values are given with 95% confidence intervals.

along the four routes  $N^{(1)}\!-\!N^{(4)}$  are given. These numbers are selected in a way, that the overall chemical equations do not contain intermediates.

Since octadecene was not present in the reaction mixture in experiments with the rhenium catalyst, its coverage can be considered low and further hydrogenation fast. Based on quasi-equilibrium adsorption of reactants and products, the following expressions can be written, respectively, for active sites

$$\theta_{SA} = K_1 C_{SA} \theta_V; \quad \theta_{AD} = K_2 C_{AD} \theta_V; \quad \theta_{AC} = K_3 C_{AC} \theta_V; \theta_{OD} = K_4 C_{OD} \theta_V$$
(1)

where  $K_1$ , etc. are the equilibrium constant of respective equilibrium steps A1–A4,  $C_{SA}$ , etc., are concentrations and  $\theta_V$  is the coverage of the vacant sites.

		Basic	routes		
Elementary steps		N <sup>(2)</sup>	N <sup>(3)</sup>	N <sup>(4)</sup>	
$SA + * \equiv SA *$	1	0	0	0	(A1)
$SA^* + H_2 \rightarrow SAH_2^*$	1	0	0	0	(R1)
$SAH_2^* \rightarrow AD^* + H_2O$	1	0	0	0	(R1')
$AD + * \equiv AD *$	-1	1	0	0	(A2)
$AD^* + H_2 \rightarrow ADH_2^*$	0	1	0	0	(R2)
$ADH_2^* \rightarrow AC^*$	0	1	0	0	(R2')
$AC + * \equiv AC *$	0	-1	1	0	(A3)
$AC^* \rightarrow OE^* + H_2O$	0	0	1	0	(R3)
$OE^* + H_2 \rightarrow OEH_2^*$ fast	0	0	1	0	(R3')
$OEH_2^* \rightarrow OD^*$ fast	0	0	1	0	(R3'')
$OD + * \equiv OD*$	0	0	-1	0	(A4)
$AC + SA \Leftrightarrow SS$	0	0	0	1	(R4)

 $N^{(1)}: SA + H_2 = AD + H_2O; N^{(2)}: AD + H_2 = AC; N^{(3)}: AC + H_2 = OD + H_2O;$ 

 $N^{(4)}$ : AC + SA = SS,



Fig. 10. Comparison for experimentally observed data and model predictions for stearic acid, aldehyde and alcohol: (a) 180 °C, 2 MPa; (b) 200 °C, 2 MPa; (c) 220 °C, 2 MPa; (d) 200 °C, 3 MPa and (e) 200 °C, 4 MPa.

From the balance equations for different types of sites, coverage of vacant sites can be easily computed

$$\theta_V = \frac{1}{1 + K_1 C_{SA} + K_2 C_{AD} + K_3 C_{AC} + K_4 C_{OD}}$$
(2)

The reaction rate  $r^{(1)}$  along the first route N<sup>(1)</sup> is defined through step R1 which can be considered as the one limiting the rate in this route

$$r^{(1)} = \frac{k_1 K_1 C_{SA} C_{H_2}}{1 + K_1 C_{SA} + K_2 C_{AD} + K_3 C_{AC} + K_4 C_{OD}}$$
(3)

The rates along the second and the third routes are given in a similar fashion

$$r^{(2)} = \frac{k_2 K_2 C_{AD} C_{H_2}}{1 + K_1 C_{SA} + K_2 C_{AD} + K_3 C_{AC} + K_4 C_{OD}}$$
(4)

$$r^{(3)} = \frac{k_3 K_3 C_{AC}}{1 + K_1 C_{SA} + K_2 C_{AD} + K_3 C_{AC} + K_4 C_{OD}}$$
(5)

The route N<sup>(4)</sup> is considered as a non-catalytic, therefore

$$r^{(4)} = k_4 C_{AC} C_{SA} \tag{6}$$

Initially, this step was considered as reversible; however, during the numerical data fitting, it turned out that the backwards reaction in the studied domain can be neglected.

Finally, the generation rates of compounds can be written as:

$$-\frac{dC_{SA}}{\rho_B dt} = r^{(1)} + r^{(4)}, \quad \frac{dC_{AD}}{\rho_B dt} = r^{(1)} - r^{(2)}; \quad \frac{dC_{AC}}{\rho_B dt} = r^{(2)} - r^{(3)} - r^{(4)};$$

$$\frac{dC_{OD}}{\rho_B dt} = r^{(3)}, \quad \frac{dC_{SS}}{dt} = r^{(4)}$$
(7)

where *t* is time and  $\rho_B$  is the mass-of-catalyst-to-liquid-volume ratio.

The temperature dependence of the rate constants was assumed according to the Arrhenius equation, while negligible influence of temperature on  $K_{SA}$  was supposed. The kinetic modelling was performed for all reaction rates and reaction sets together. For the parameter estimation instead of absolute values of product concentrations, their molar percentage was used, and a set of differential equations describing the changes in the concentrations profiles of the reagents and products with time was solved by means of ModEst software [20]. Using Levenberg–Marquardt simplex method, the target function, which was defined as incompliance between the experimental and calculated values of concentrations, was used to solve the system. The sum of the residual squares between the model and the experimental data was minimized using the following objective function:

$$Q = \|x_{exp} - x_{est}\|^2 = \sum_{t} \sum_{i} (x_{exp,it} - x_{est,it})^2$$
(8)

where  $x_{exp}$  is the experimental value,  $x_{est}$  denotes the predictions given by the model, *i* is the component index and *t* is the time value. The quality of the fit and accuracy of the model description was defined by the degree of explanation  $R^2$ ; which reflects comparison between the residuals given by the model to the residuals of the simplest model one may think of, i.e., the average value of all the data points. The  $R^2$  value is given by the expression

$$R^{2} = 100 \frac{\left(y_{model} - y_{experiment}\right)^{2}}{\left(y_{model} - \bar{y}_{experiment}\right)^{2}}$$
(9)

Preliminary calculations demonstrated that the values of equilibrium constants  $K_3$  and  $K_4$  are small enough to neglect them. Since the concentration of aldehyde is also low, the term  $K_2C_{AD}$  was neglected. Thus the values of  $k_2$  and  $k_3$  in fact are lumped ones, containing also the value of  $K_2$  and  $K_3$ , respectively.

The values of the calculated frequency factors, activation energy and adsorption constants as well as the estimated relative standard errors (in%) of the tested reaction mechanism are presented in Table 4. The values of pre-exponential constants for  $k_1$ - $k_3$  also include the catalyst concentration.

Fig. 10 displays as, an example, an excellent comparison for experimentally observed data and model predictions for reactants in the studied range of pressures, concentrations and temperature with the degree of explanation 99.72%. The standard errors of all parameters are acceptably low.

The values of activation energies for selective hydrogenation of acids to alcohols are not readily available for Re-based catalysts, thus a comparison can be made only with other types of catalysts, such as homogeneous catalytic hydrogenation with Cu oleates giving 56 kJ/mol [21].

The kinetic model, presented above, was developed for the case of first order in hydrogen, which implies weak adsorption of hydrogen on the catalyst surface. It can be thus probably applied for similar catalytic systems as applied in the current work when, for example, oxophilic metals are used on reducible oxides or even non-reducible oxides. For reducible metals, such as Pt or a combination of reducible and oxophilic metals, such as ReOx–Pd/SiO<sub>2</sub> catalyst utilized for hydrogenation of saturated fatty acids [22], some modifications of the kinetic model might be needed to address changes in hydrogen adsorption behaviour and possible different kinetic regularities.

# 4. Conclusions

Highly dispersed  $\text{ReO}_{\star}/\text{TiO}_2$  was applied as a catalyst for the selective hydrogenation of fatty acids to alcohols. The selectivity to octadecane up to 93% was achieved in the temperature range between 180–220 °C and 2–4 MPa of total pressure.

It was demonstrated that with a decrease of temperature and an increase of pressure, a higher selectivity to the main product is achieved. A high yield of octadecanol was obtained due to a strong adsorption of the fatty acid compared to the fatty alcohol, which inhibits a further transformation of the alcohol to alkanes. The hydrocarbon can be treated as the only by-product of the reaction, since stearyl stearate, which is also formed, can be further transformed to the desired products. Moreover, with pre-reduced 4% ReO<sub>x</sub>/TiO<sub>2</sub>, the selectivity to hydrocarbons is around 5%. However, after a complete conversion of stearic acid, hydrocarbons were mainly formed with octadecane as the main product.

The XPS studies confirm that the oxidation state of rhenium was Re<sup>4+</sup> and Re<sup>6+</sup> during the experiments. In experiments with a non-reduced rhenium catalyst, a lower conversion was obtained with a higher formation of hydrocarbons, which was caused by a lower amount of oxygen vacancies on the interface between rhenium and titania.

The reaction kinetics was modelled based on the mechanistic considerations for stearic acid hydrogenation. The calculated results were compared with experimental data through numerical data fitting, showing a very good correspondence was obtained (with the degree of explanation close to 99.6%).

### Acknowledgments

This work is a part of activities of Åbo Akademi Process Chemistry Centre (PCC). The authors would like to acknowledge Markus Peurla from Laboratory of Electron Microscopy at University of Turku for performing TEM analysis and Sten Linholm from Laboratory of Analytical Chemistry at Åbo Akademi for performing ICP– OES analysis. Moreover, financial support from Åbo Akademi University Endowment is gratefully acknowledged and EPSRC as part of the CASTech grant (EP/G011397/1).

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