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# Controlling hydrodeoxygenation of stearic acid to *n*-heptadecane and *n*-octadecane *via* chemical properties of Ni/SiO<sub>2</sub>-ZrO<sub>2</sub>

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**Abstract:** A series of SiO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide with varying SiO<sub>2</sub> concentrations was hydrothermally synthesized and used as support for Ni in the hydrodeoxygenation of stearic acid. ZrO<sub>2</sub> provides a relatively low surface area and only Lewis acid sites, and Ni supported on ZrO<sub>2</sub> produces *n*-heptadecane from stearic acid via hydrogenation and decarbonylation. The SiO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides have a higher specific surface area as well as a novel spherical and nano-layer shaped morphology. Brønsted acid sites are created by incorporation of SiO<sub>2</sub> into ZrO<sub>2</sub> promoting the hydrodeoxygenation activity of Ni and specifically opening a new reaction route to *n*-octadecane via the dehydration of 1-octadecanol intermediate into 1-octadecene with subsequent hydrogenation.

#### Introduction

The high growth rates and oil content, as well as the independence from arable land make microalgae the ideal basis for third-generation biofuels.<sup>[1]</sup> The conversion of algae oil into hydrocarbon transportation fuel requires removing of oxygen from triglycerides. This can be achieved using commercially available sulfide catalysts, e.g., NiMoS/Al<sub>2</sub>O<sub>3</sub>, and existing hydrotreating infrastructure.<sup>[2]</sup> However, the sulfide catalysts are not ideal for the conversion of the nearly sulfur-free triglycerides, because they deactivate via sulfur elimination and contaminate the product stream with organic sulfides.<sup>[3]</sup>

Supported noble metal Ru, Pd and Pt catalysts overcome such disadvantages offering high activity and selectivity for hydrodeoxygenation of triglycerides and fatty acids, but are rather expensive.<sup>[4]</sup> A more economic alternative would be tungsten carbide based catalysts however, their performance has not been able to reach the performance of commercial hydrotreating catalysts (NiMo/Al<sub>2</sub>O<sub>3</sub>).<sup>[5]</sup>

We have developed two types of novel sulfur-free Ni based catalysts to directly convert microalgae oil to diesel-range hydrocarbons at 260 °C and 40 bar  $H_2$ .<sup>[6]</sup> The catalytic process

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starts with fast hydrogenolysis into propane and fatty acids followed by slower hydrodeoxygenation of the fatty acids into alkanes.<sup>[6a]</sup> The conversion of fatty acids, e.g., stearic acid, on Ni/ZrO<sub>2</sub> occurs via two pathways, one catalyzed solely by Ni and one catalyzed synergistically by Ni and the ZrO<sub>2</sub> support, both leading to an alkane with one carbon less than the fatty acid, i.e. *n*-heptadecane (C<sub>17</sub>) from stearic acid (C<sub>18</sub>). On Ni, the fatty acid is hydrogenated to the aldehyde, followed by decarbonylation of the aldehyde to an alkane. On ZrO<sub>2</sub>, α-H abstraction and elimination of H<sub>2</sub>O from the fatty acid adsorbed on the oxygen vacancies leads to a ketene intermediate, which is further hydrogenated to an aldehyde that decarbonylates to an alkane on Ni.<sup>[7]</sup>

Generally, ZrO<sub>2</sub> is an excellent catalytic support, inter alia due to its high hydrothermal stability.<sup>[8]</sup> The relatively low specific surface area poses some drawbacks, as the sites involved in the hydrodeoxygenation pathway on ZrO<sub>2</sub> contribute markedly to the overall conversion. The incorporation of SiO<sub>2</sub> has been reported to enhance the specific surface area of ZrO<sub>2</sub> <sup>[9]</sup> through formation of a mixed oxide phase, and can additionally induce Brønsted acid sites.<sup>[10]</sup> It has been shown previously that the presence of Brønsted acid sites in proximity to Ni in zeolites enhances the hydrogenation activity.<sup>[11]</sup>

Therefore, we explored the general applicability of the concept of rate enhancement by introducing Brønsted acid sites via SiO<sub>2</sub>- $ZrO_2$  mixed oxides on the support for Ni with respect to the hydrodeoxygenation of stearic acid, one of the most abundant fatty acids from algae oil. It was hypothesized that the combination of the large pore Brønsted acid support with Ni as hydrogenation catalyst function may lead to high activity and high selectivity retaining all carbon atoms in the fatty acid.

#### **Results and Discussion**

The catalytic properties of two types of Ni catalysts, prepared by wet impregnation on hydrothermally synthesized and impregnated SiO<sub>2</sub>-ZrO<sub>2</sub> supports are investigated. For details of the preparation procedure please see experimental part.

#### Catalyst characterization

The X-ray powder diffractogram (XRD) of the  $ZrO_2$  samples, prepared by the hydrothermal synthesis (H), are presented in **Figure 1**. The diffractogram of unmodified monoclinic  $ZrO_2$  (*m*- $ZrO_2$ ) with its characteristic diffraction pattern is shown as well for comparison. It shows the expected diffraction peaks at 24.5, 28.3, 31.6 and 34.5° with a shoulder at 35.3° (JCPDS card

No. 37-1484).<sup>[12]</sup> With increasing SiO<sub>2</sub>-content, the peak intensity (6 SiO<sub>2</sub>-ZrO<sub>2</sub> (H)) decreased, suggesting lower crystallinity. In parallel, the crystal phase of ZrO<sub>2</sub> changed from monoclinic to a new phase (27 SiO<sub>2</sub>-ZrO<sub>2</sub> and 37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H)), which has been assigned to tetragonal ZrO<sub>2</sub> in literature <sup>[12c, 12d]</sup>. Above 40 wt% SiO<sub>2</sub>, only broad signals characteristic for amorphous oxides<sup>[13]</sup> were observed, while diffraction peaks of either monoclinic or tetragonal ZrO<sub>2</sub> were absent, implying an amorphous structure of the resulting materials<sup>[14]</sup>. In line with that, the peak attributed to pure SiO<sub>2</sub> was lowered in intensity. Presumably, this is the result of atomic dispersion in mixed SiO<sub>2</sub>-ZrO<sub>2</sub> where Zr-O units are alternating with SiO<sub>4</sub>-tetrahedra. In contrast, the diffraction patterns remain identical when the ZrO<sub>2</sub> is modified by impregnation with SiO<sub>2</sub> (**Figure 2**).



Figure 1. XRD patterns of  $ZrO_2$  modified with increasing concentrations of SiO<sub>2</sub> by the hydrothermal method. A) 0 - 37 mol% SiO<sub>2</sub>. B) 49 - 100 mol% SiO<sub>2</sub>.



Figure 2. XRD patterns of  $ZrO_2$  modified with increasing amount of SiO<sub>2</sub> by impregnation method (0 – 29 mol%).

#### High Resolution Scanning Electron Microscopy (HR-SEM)

The highly increased specific surface area of the materials prepared by the hydrothermal method is also manifested in the HR-SEM micrographs. While unmodified ZrO<sub>2</sub> (Figure 3, upper left) showed particles with several micrometers in diameter, the surface of ZrO<sub>2</sub>-SiO<sub>2</sub> is more facetted, forming nano-layers with increasing content of SiO<sub>2</sub>. For 37 SiO<sub>2</sub>-ZrO<sub>2</sub>, highly organized structures with a primary particle size of 1 µm are formed. Nano layers arrange in a way that spheres with sponge like morphologies are formed. Similar structures were reported by Faria et al.<sup>[15]</sup> The 67 ZrO<sub>2</sub>-SiO<sub>2</sub> had an extraordinary morphology, in which the excess SiO<sub>2</sub> not incorporated into ZrO<sub>2</sub> was deposited on the surface of the lamellar structure as SiO<sub>2</sub>nanoparticles with a size of 10 nm (Figure 3, bottom right). In contrast, the SiO<sub>2</sub> impregnated ZrO<sub>2</sub> samples did not show such a change in morphology and were comparable in shape to the reference material independent of the degree of the SiO<sub>2</sub> loading (Figure 4). The silica deposits are visible on the ZrO<sub>2</sub> surface.

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Figure 3. High resolution scanning electron microscopy (HR-SEM) images of untreated ZrO<sub>2</sub> (0 mol% SiO<sub>2</sub>), 6 SiO<sub>2</sub>-ZrO<sub>2</sub>, 27 SiO<sub>2</sub>-ZrO<sub>2</sub>, 37 SiO<sub>2</sub>-ZrO<sub>2</sub>, 67 SiO<sub>2</sub>-ZrO<sub>2</sub> prepared by *one-pot* hydrothermal method.



Figure 4. HR-SEM images of untreated  $ZrO_2$  (0 mol% SiO<sub>2</sub>) and  $ZrO_2$  impregnated with SiO<sub>2</sub> at increasing loadings.

#### **Physicochemical properties**

As shown in **Table 1**, with the increase of SiO<sub>2</sub> concentration, the BET surface areas of the Ni/SiO<sub>2</sub>-ZrO<sub>2</sub>, determined by N<sub>2</sub> physisorption, increased from 72 m<sup>2</sup>·g<sup>-1</sup> for Ni/*m*-ZrO<sub>2</sub> to 193 m<sup>2</sup>·g<sup>-1</sup> for Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub>, significantly higher than reported before,<sup>[16]</sup> while it afterwards decreased to 67 m<sup>2</sup>·g<sup>-1</sup> for Ni/67 SiO<sub>2</sub>-ZrO<sub>2</sub>, which is close to the value for Ni/SiO<sub>2</sub>. The high BET surface area for Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub> (193 m<sup>2</sup>·g<sup>-1</sup>) is due to the small crystal size, which was only 2.5 nm compared to 7.1 nm of *m*-ZrO<sub>2</sub> (**Table S1**). In contrast, the catalysts prepared by the SiO<sub>2</sub>-*impregnation* method only had specific surface areas between 71 – 97 m<sup>2</sup>·g<sup>-1</sup> (**Table 2**).

Table 1. Physicochemica	I properties of SiO <sub>2</sub> modified	d Ni/ZrO <sub>2</sub> catalysts	(one-pot hydrothermal).	
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Catalyst <sup>[a]</sup>	Sbet	wt% Ni <sup>[b]</sup>	$D^{[c]}$	d(c)	Concentration of acid sites <sup>[d]</sup>	Concentration of basic sites <sup>[e]</sup>
	[m <sup>2</sup> ·g <sup>-1</sup> ]	[%]	[%]	[nm]	[ <i>m</i> mol·g <sup>-1</sup> ]	[ <i>m</i> mol⋅g <sup>-1</sup> ]
Ni/ZrO <sub>2</sub>	72	9.7	2.9	35	0.15	0.30
Ni/6 SiO <sub>2</sub> -ZrO <sub>2</sub>	122	9.4	2.5	41	0.23	0.25
Ni/27 SiO <sub>2</sub> -ZrO <sub>2</sub>	128	9.8	1.8	57	0.34	0.23
Ni/37 SiO <sub>2</sub> -ZrO <sub>2</sub>	193	10	1.7	61	0.28	0.12
Ni/49 SiO <sub>2</sub> -ZrO <sub>2</sub>	141	9.8	1.9	52	0.24	0.10
Ni/61 SiO <sub>2</sub> -ZrO <sub>2</sub>	111	9.8	2.1	49	0.19	0.09
Ni/67 SiO <sub>2</sub> -ZrO <sub>2</sub>	67	10	2.5	40	0.11	0.06
Ni/SiO <sub>2</sub>	75	9.5	3.8	27	0	0

[a] Number in the label is mol% SiO<sub>2</sub>. [b] Determined by Ni-AAS. [c] Dispersion (*D*) and particle size (*d*) were determined by H<sub>2</sub>-Chemisorption. [d] Determined by TPD of NH<sub>3</sub>. [e] Determined by TPD of CO<sub>2</sub>.



Table 2. Physicochemical properties of SiO2 impregnated Ni/ZrO2 catalysts.							
Catalyst <sup>[a]</sup>	Catalyst <sup>[a]</sup> S <sub>BET</sub> wt% Ni <sup>[b]</sup> D <sup>[c]</sup> d <sup>[c]</sup> Concentration of Concentrat		Concentration of basic sites [e]				
	[m <sup>2</sup> ·g <sup>-1</sup> ]	[%]	[%]	[nm]	[ <i>m</i> mol·g <sup>-1</sup> ]	[ <i>m</i> mol·g <sup>-1</sup> ]	
Ni/ZrO <sub>2</sub>	72	9.7	2.9	35	0.15	0.30	
Ni/4 SiO <sub>2</sub> -ZrO <sub>2</sub>	71	10	3.0	33	0.16	0.19	
Ni/16 SiO <sub>2</sub> -ZrO <sub>2</sub>	86	9.7	3.1	33	0.16	0.14	
Ni/29 SiO <sub>2</sub> -ZrO <sub>2</sub>	97	9.9	3.6	28	0.16	0.10	

[a] Number in the label is mol% SiO<sub>2</sub>. [b] Determined by Ni-AAS. [c] Dispersion (*D*) and particle size (*d*) were determined by H<sub>2</sub>-Chemisorption. [d] Determined by TPD of NH<sub>3</sub>. [e] Determined by TPD of CO<sub>2</sub>.

The concentration of acid sites were always lower for the Niimpregnated catalysts than for the parent supports (compare **Table 1** with **S1** and **Table 2** with **S2**). The acid site concentration increased from 0.15 to 0.34 mmol·g<sup>-1</sup> for Ni/ZrO<sub>2</sub> to Ni/27 SiO<sub>2</sub>-ZrO<sub>2</sub> (H) and decreased to 0 for Ni/SiO<sub>2</sub> (**Table 1**). The concentration of acid sites for the Ni-catalysts, modified by SiO<sub>2</sub>-impregnation was constant at 0.16 mmol·g<sup>-1</sup> (**Table 2**) and was lower than that of the corresponding parent support (**Table S2**). This indicates that the ZrO<sub>2</sub> surface and its acid sites are partially blocked by SiO<sub>2</sub>. With the increase of the SiO<sub>2</sub> content, the basic site concentration for the mixed oxides prepared with the hydrothermal method decreased from 0.25 to 0 mmol·g<sup>-1</sup>, and that for the SiO<sub>2</sub> impregnated samples decreased from 0.19 to 0.10 mmol·g<sup>-1</sup>, in line with similar studies on SiO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides by Yamaguchi *et al.*<sup>[17]</sup>.

#### IR spectra of adsorbed pyridine

In Figure 5 the IR spectra of adsorbed pyridine are shown for unmodified monoclinic ZrO<sub>2</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub> (37 SiO<sub>2</sub>-ZrO<sub>2</sub>, H), SiO<sub>2</sub>impregnated ZrO<sub>2</sub> (29 SiO<sub>2</sub>-ZrO<sub>2</sub>, Imp.) and a pure SiO<sub>2</sub> reference. The ZrO<sub>2</sub> showed the bands of pyridine adsorbed on Lewis acid sites (LAS) at 1610 and 1448 cm<sup>-1</sup> (Figure 5, A). SiO<sub>2</sub>-ZrO<sub>2</sub> showed emerging peaks at 1630 and 1547 cm<sup>-1</sup> attributed to pyridinium ions formed by adsorption on Brønsted acid sites (BAS). The band at 1462 cm<sup>-1</sup> is attributed to pyridine coordinately adsorbed on Lewis acid sites (LAS), the band at 1491 cm<sup>-1</sup> to pyridine adsorbed on both strong LAS and BAS.<sup>[18]</sup> Table 3 shows the quantification of BAS and LAS for 27 SiO<sub>2</sub>-ZrO<sub>2</sub> (H) and 37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H). 27 SiO<sub>2</sub>-ZrO<sub>2</sub> (H) had the highest total concentration of acid sites (0.93 mmol·g<sup>-1</sup>), and 37 SiO<sub>2</sub>- $ZrO_2$  (H) has the highest concentration of BAS (0.36 mmol·g<sup>-1</sup>). In contrast, the impregnated material (29 SiO<sub>2</sub>-ZrO<sub>2</sub>, Imp.) showed adsorption on identical sites as on ZrO2, but in lower concentrations. This is attributed to the fact that ZrO<sub>2</sub> is partially covered by SiO<sub>2</sub>, leading to fewer accessible Lewis acid sites. Finally, the pure SiO<sub>2</sub> reference did not adsorb significant concentrations of pyridine after evacuation at 150°C.

The broad peaks at 3774 and  $3680 \text{ cm}^{-1}$  (**Figure 5, B**) are assigned to the stretching vibrations of terminal and bridging surface OH groups of Zr, respectively, that disappear upon adsorption of pyridine and are visible as negative peaks in the

difference spectra.<sup>[16b, 18d, 19]</sup> The band at  $3735 \text{ cm}^{-1}$  (37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H) and 29 SiO<sub>2</sub>-ZrO<sub>2</sub> Imp.) is attributed to isolated SiOH groups.<sup>[18a, 20]</sup>



**Figure 5.** IR spectra of pyridine adsorbed on  $ZrO_2$  (black), 37 SiO<sub>2</sub>-ZrO<sub>2</sub> (*one-pot* hydrothermal synthesis) in orange, 29 SiO<sub>2</sub>-ZrO<sub>2</sub> (*Impregnation*) in blue and SiO<sub>2</sub> reference (gray). **A)** Pyridine vibrations region (1700 – 1400 cm<sup>-1</sup>) **B)** Surface Zr-OH and Si-OH stretching vibration region (3800 – 3500 cm<sup>-1</sup>).

Wavenumber [cm-1]

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Table 3. Concentration of Brønsted and Lewis acid sites quantified by IR spectra of adsorbed pyridine.						
Support/ modification	Total concentration of acid sites	Concentration of BAS	Concentration of LAS	BAS/ LAS		
	[µmol·g⁻¹]	[µmol·g⁻¹]	[µmol·g⁻¹]			
Ni/27 SiO <sub>2</sub> -ZrO <sub>2</sub>	930	136	794	0.17		
Ni/37 SiO <sub>2</sub> -ZrO <sub>2</sub>	730	356	374	0.95		

The IR spectra of adsorbed pyridine for all samples prepared by the one-pot hydrothermal synthesis method with different SiO<sub>2</sub>contents are compared in Figure 6, A. As indicated in the previous paragraph, the spectrum of bare ZrO<sub>2</sub> and 6 SiO<sub>2</sub>-ZrO<sub>2</sub> showed broad bands with low intensities at 3774 and 3680 cm<sup>-1</sup> that are attributed to ZrOH groups (Figure 6, B). For higher contents of SiO<sub>2</sub> (27 - 61 mol%), bands at 3745 - 3735 cm<sup>-1</sup> appeared that correspond to isolated SiOH groups. Like SiO<sub>2</sub>, the mixed oxide with the highest  $SiO_2$ -content (69  $SiO_2$ -ZrO<sub>2</sub>) showed negligible adsorption of pyridine. We want to highlight the peak at 3608 cm<sup>-1</sup> that only appeared for 27-SiO<sub>2</sub>-ZrO<sub>2</sub> and 37 SiO<sub>2</sub>-ZrO<sub>2</sub>, which also had the highest concentrations of BAS. This band at 3608 cm<sup>-1</sup> is similar in wavenumber to the bridging OH groups in zeolites<sup>[21]</sup> responsible for the high Brønsted acid strength. Brønsted acid sites were suggested to be present in SiO<sub>2</sub>-ZrO<sub>2</sub> as well (Scheme 1, A).<sup>[21c, 22]</sup> However, in a classic substitution model this would require a sufficient number of Zr3+-cations[23], which are unlikely to be formed under the conditions employed.<sup>[24]</sup> Therefore, we tentatively propose a structure (Scheme 1, B) based on Pauling's electrostatic valence rule.<sup>[25]</sup> The coordination number (CN) of Zr in tetragonal ZrO<sub>2</sub>, which is the dominating phase in the presence of SiO<sub>2</sub>, is eight, whereas the CN(Si) = 4 in  $SiO_2$ . The incorporation of  $SiO_2$ into the ZrO<sub>2</sub> structure and, thus, the formation of a mixed oxide lead to an under-coordination of the surface oxygen for ZrO2 rich samples. This is hypothesized to be balanced by a proton, leading to an OH band at 3608 cm<sup>-1</sup> accounting for the Brønsted acid site.<sup>[26]</sup> With increasing SiO<sub>2</sub>-content, the incorporation cannot be stabilized, resulting in phase segregation and a lower concentration of BAS.



 $\label{eq:Scheme 1.} Scheme 1. Schematic representation of bridging OH and terminal OH group of Si-O-Zr in mixed oxide SiO_2-ZrO_2.$ 



**Figure 6.** IR spectra of pyridine adsorbed on SiO<sub>2</sub>-ZrO<sub>2</sub> (*one-pot* hydrothermal synthesis) with varying mol% SiO<sub>2</sub>. **A)** Pyridine vibrations region (1700 – 1400 cm<sup>-1</sup>) **B)** Surface Zr-OH and Si-OH stretching vibration region (3800 – 3500 cm<sup>-1</sup>).

The model is derived from the considerations of Tanabe<sup>[10b]</sup>, taking into account the coordination numbers of both cations and anions. According to this model, all oxygen anions are assumed to maintain the coordination number of the major oxide component. In contrast to that, the metal cations may retain the coordination number of their pure metal oxides for both major and minor component. This leads to an excess charge in a model structure. If the excess charge is negative, it has to be balanced by a proton generating a BAS. Accordingly, a positive excess charge leads to the introduction of an oxygen vacancy, and hence to a LAS. The simultaneous occurrence of BAS and LAS, like here, may point to the existence of domains with varying concentrations of the constituents.<sup>[27]</sup> Note that such a model is in agreement with the Sanderson electronegativity concept<sup>[28]</sup> and the mixing rule<sup>[29]</sup>.

#### <sup>29</sup>Si-NMR Spectroscopy

The SiO<sub>2</sub>-modified sample (**Figure 7**) prepared by the *one-pot* hydrothermal method (*e.g.* 37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H)) shows two peaks with chemical shifts of -83 ppm and -96 ppm, that represent a 2-fold (Q2) and 3-fold (Q3) coordination of Si-atoms as in  $Si(OSi)_2(OZr)_2$  and  $Si(OSi)_3(OZr)_1$  or  $Si(OSi)_2(OH)_2$  and  $Si(OSi)_3(OH)_1$ , respectively.<sup>[14, 30]</sup> Si-O-H and Si-O-Zr bonds are

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not distinguishable in <sup>29</sup>Si-NMR.<sup>[22a]</sup> This allows us to conclude that SiO<sub>2</sub> and ZrO<sub>2</sub> exist in dispersed form in a mixed oxide. In contrast, the spectrum of the 29 SiO<sub>2</sub>-ZrO<sub>2</sub> (*Imp.*) showed a broad signal at -114 ppm corresponding to Q4, the 4-fold coordination of siloxane bonds Si(OSi)<sub>4</sub>. This points to the fact that the SiO<sub>2</sub> phase and the ZrO<sub>2</sub> phase are partially segregated. Thus, we conclude that SiO<sub>2</sub> forms a mixed oxide phase with ZrO<sub>2</sub> through a hydrothermal synthesis, whereas it is only deposited onto the ZrO<sub>2</sub> support by the *impregnation* method. With increasing SiO<sub>2</sub> concentration these peaks are shifted towards lower field, due to the coordination of Si with Si increases (**Figure S1**).



Figure 7. <sup>29</sup>Si-MAS-NMR spectra of ZrO<sub>2</sub>, 37 SiO<sub>2</sub>-ZrO<sub>2</sub> (*one-pot* hydrothermal) and 29 SiO<sub>2</sub>-ZrO<sub>2</sub> (*Impregnation*).



Hydrodeoxygenation of stearic acid

Scheme 2. Proposed reaction network for the hydrodeoxygenation of stearic acid, showing the decarbonylation route towards *n*-heptadecane (C<sub>17</sub>), dehydration/hydrogenation to *n*-octadecane (C<sub>18</sub>) and reversible esterification towards stearyl stearate.<sup>[6b, 7, 31]</sup>

Catalytic hydrodeoxygenation of stearic acid was carried out on the Ni/SiO<sub>2</sub>-SiO<sub>2</sub> catalysts. As shown in Figure 8, the initial conversion of stearic acid on Ni/37 SiO2-ZrO2 (H) resulted in 1-octadecanol as primary product, formed by the hydrogenation of the fatty acid (Figure 9, B).[6a] Further conversion led to the appearance of secondary product, stearyl stearate ester, n-heptadecane (C17) and n-octadecane (C18). Stearyl stearate was formed through esterification of 1-octadecanol with stearic acid.<sup>[6b, 32]</sup> This reaction is reversible and stearyl stearate reached a maximum at 8 h and decayed afterwards until depletion after 20 h. Only alkane products, n-heptadecane and n-octadecane, remained after 24 h. n-Heptadecane was formed via dehydrogenation of the 1-octadecanol intermediate to 1-octadecanal with subsequent decarbonylation, and n-octadecane was formed via dehydration of 1-octadecanol to 1-octadecene with subsequent hydrogenation (Scheme 2).



**Figure 8.** Product distribution for the hydrodeoxygenation of stearic acid over 10 wt% Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H) as a function of time, stearic acid (•), 1-octadecanol ( $\blacktriangle$ ), *n*-heptadecane (•), *n*-octadecane (•) and stearyl stearate (x). Reaction conditions: stearic acid (0.5 g), 0.05 g 10 wt% Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H), dodecane (100 mL), 260 °C, p(H<sub>2</sub>) = 40 bar, stirring at 600 rpm, 8 h.

**Figure 10** shows the Turnover frequency (TOF) of stearic acid and the concentration of BAS as a function of SiO<sub>2</sub>-content for Ni/ZrO<sub>2</sub>–SiO<sub>2</sub> (H) catalysts. Ni/ZrO<sub>2</sub> has a TOF of 64 (conversion rate of 3.2 *m*mol·g<sub>cat</sub>·1·h<sup>-1</sup>). With increasing SiO<sub>2</sub>-content, the TOF increased. The TOF of 297 (conversion rate of 8.6 *m*mol·g<sub>cat</sub>·1·h<sup>-1</sup>) for Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H) was the highest TOF (**Figure 9, A** and **Figure 10**), decreasing with further increasing SiO<sub>2</sub> content (**Table S3**). This trend is in line with the variation of BAS concentrations and the specific surface area of the catalysts. The conversion rate of stearic acid on Ni follows approximately the concentration of BAS from the SiO<sub>2</sub>-ZrO<sub>2</sub> support (**Figure 10**), indicating a promotion of hydrogenation activity of Ni by close BAS. Similar observations were made for hydrodeoxygenation of phenolic substrates by Song *et al.*<sup>[11]</sup>

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enhanced by  $ZrO_2$ ,<sup>[7]</sup> the markedly higher specific surface area may also contribute to the activity (**Figure S2**). In contrast, hydrodeoxygenation of stearic acid over SiO<sub>2</sub>-impregnated Ni/ZrO<sub>2</sub> catalysts showed a decrease of conversion rate with increasing SiO<sub>2</sub>-content from 3.2 *m*mol·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup> for Ni/ZrO<sub>2</sub> to 1.4 *m*mol·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup> for Ni/29 SiO<sub>2</sub>-ZrO<sub>2</sub> (*Imp.*) (**Figure S3**, **A** and **Table S4**). The products evolving with increasing stearic acid conversion is similar to that on Ni/ZrO<sub>2</sub>. The decrease in activity is attributed to the SiO<sub>2</sub> partly covering ZrO<sub>2</sub>, reducing so the accessible ZrO<sub>2</sub> surface.<sup>[6a, 7]</sup>



**Figure 9. A)** Conversion of stearic acid as a function of time. **B)** Yields of 1-octadecanol, stearyl stearate, *n*-heptadecane and *n*-octadecane over Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub> (*one-pot* hydrothermal) as a function of stearic acid conversion. 1-octadecanol ( $\blacktriangle$ ), *n*-heptadecane ( $\blacklozenge$ ), *n*-octadecane ( $\blacksquare$ ) and stearyl stearate ( $\times$ ). Reaction conditions: stearic acid (0.5 g), Ni/SiO<sub>2</sub>-ZrO<sub>2</sub> catalyst (10 wt% Ni, 0.05 g), dodecane (100 mL), 260 °C, *p*(H<sub>2</sub>) = 40 bar, stirring at 600 rpm, 2 h.



**Figure 10.** Turnover frequency (TOF) for the hydrodeoxygenation of stearic acid and concentration of Brønsted acid sites as a function of SiO<sub>2</sub>-content in the Ni/SiO<sub>2</sub>-ZrO<sub>2</sub> catalyst prepared by the hydrothermal method. Reaction conditions: stearic acid (0.5 g), Ni/SiO<sub>2</sub>-ZrO<sub>2</sub> catalyst (10 wt% Ni, 0.05 g), dodecane (100 mL), 260 °C,  $p(H_2) = 40$  bar, stirring at 600 rpm, 2 h.

It is noticeable that on Ni/ZrO2 catalyst, n-heptadecane was the dominant hydrocarbon product at full conversion and the n-octadecane yield was negligible,<sup>[31]</sup> while on Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub> (H), octadecane had a yield as high as 60%. Bare ZrO<sub>2</sub> only possesses LAS, whereas the presence of BAS in (H) catalysts enhanced the rate of 1-octadecanol dehydration, causing a shift in selectivity towards n-octadecane. This shift in product distribution from n-heptadecane to n-octadecane is advantageous from a carbon-economy point of view.[6a, 33] In Figure 11 the rate constants for the dehydration of 1-octadecanol leading to C18 and esterification of stearic acid with C18-OH leading to stearyl stearate are shown. The rate constants for both reactions have a positive correlation with the BAS concentrations on the catalysts, indicating Brønsted acidic proton as the active site. Obviously, the conversion of stearic acid over Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub> has the highest yield of n-octadecane, because it has the highest concentration of Brønsted acid sites.



**Figure 11.** Rate constant for the dehydration of 1-octadecanol (**•**) and esterification of stearic acid and 1-octadecanol (**x**) normalized to catalyst weight as a function of concentration of BAS on Ni/SiO<sub>2</sub>-ZrO<sub>2</sub> catalyst. Reaction conditions: stearic acid (0.5 g), Ni/SiO<sub>2</sub>-ZrO<sub>2</sub> catalyst (10 wt% Ni, 0.05 g), dodecane (100 mL), 260 °C,  $p(H_2) = 40$  bar, stirring at 600 rpm, 2 h.

## Conclusions

Hydrothermal synthesis of SiO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides led to materials with a maximum in Brønsted acid site concentration at approximately 40 mol% of SiO<sub>2</sub> and 60 mol% ZrO<sub>2</sub>. Brønsted acid sites are concluded to be induced by the substitution in oxide lattices differing in the coordination of the cations, Si4+ and Zr<sup>4+</sup>. Differences in morphology resulted in high specific surface areas of these mixed oxides, having a spherical morphology with agglomerates of nano-layered materials. The higher concentration of Brønsted acid sites and higher specific surface area led to a maximum in the catalytic activity for stearic acid deoxygenation for Ni/37 SiO<sub>2</sub>-ZrO<sub>2</sub>. Remarkably, an increase in the rates of hydrogenation reactions by neighboring Brønsted acid sites and Ni particles was observed. While the high Brønsted acid site concentration facilitates the dehydration of 1-octadecanol intermediate, which leads to an enhanced n-octadecane formation.

### **Experimental Section – Materials and Methods**

**Chemicals:** All chemicals were purchased commercially: ZrO(NO<sub>3</sub>)<sub>2</sub> × x H<sub>2</sub>O (Sigma-Aldrich, 99%), urea (Sigma-Aldrich ACS reagent, 99.0-100.5%), LUDOX TM-40 (40 wt% SiO<sub>2</sub>-suspension, Sigma-Aldrich), Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (Acros Organics, ≥98.5%), stearic acid (Sigma-Aldrich, ≥99.5% analytical standard), 1-octadecanol (Sigma-Aldrich, ≥99.5% Selectophore<sup>TM</sup>), *n*-octadecane (Sigma-Aldrich, 99%), *n*-heptadecane (Sigma-Aldrich, 99%), dodecane (Sigma-Aldrich, ≥99%, *ReagentPlus*).

**Catalyst preparation:** Silica modified ZrO<sub>2</sub> supports with various SiO<sub>2</sub>content were prepared by two different methods (**Table 4**). For the first pathway a hydrothermal synthesis route in the presence of ZrO<sub>2</sub> and a SiO<sub>2</sub> precursor was chosen. Various amount of LUDOX TM-40 (colloidal SiO<sub>2</sub>-suspension), 44.4 g ZrO(NO<sub>3</sub>)<sub>2</sub> • x H<sub>2</sub>O and urea were dissolved in bi-distilled water according to **Table S5** (see **Supporting Information**). The solution was transferred to a stainless steel autoclave with a Teflon® liner. Herein, at 180 °C and autogenous pressure a precipitate was formed after 24 h. Therefore, this procedure is called *one-pot* hydrothermal method (H). After washing the precipitate with H<sub>2</sub>O five times, it was dried overnight at 110 °C and then ground and calcined in synthetic air at 400 °C for 4 h at a heating rate of 2 °C·min<sup>-1</sup> (flow rate: 100 mL·min<sup>-1</sup>). The labeling of both catalysts as well as supports corresponds to the mol% of SiO<sub>2</sub>, derived from Si elemental analysis by ICP-OES.



<b>Table 4.</b> Overview of all $SiO_2$ - $ZrO_2$ supports prepared by twodifferent methods.							
Catalyst <sup>[a]</sup>	mol% SiO2	mol% Si	mol% ZrO <sub>2</sub>	mol% Zr			
ZrO <sub>2</sub>	<1	<1	100	33			
6 SiO <sub>2</sub> -ZrO <sub>2</sub> (H)	6	2.1	94	31			
27 SiO <sub>2</sub> -ZrO <sub>2</sub> (H)	27	9.0	73	24			
37 SiO <sub>2</sub> -ZrO <sub>2</sub> (H)	37	13	63	21			
49 SiO <sub>2</sub> -ZrO <sub>2</sub> (H)	49	16	51	17			
61 SiO <sub>2</sub> -ZrO <sub>2</sub> (H)	61	20	39	13			
67 SiO <sub>2</sub> -ZrO <sub>2</sub> (H)	67	22	33	11			
SiO <sub>2</sub>	99	33	<1	<1			
4 SiO <sub>2</sub> -ZrO <sub>2</sub> (Imp.)	4	1.4	96	32			
16 SiO <sub>2</sub> -ZrO <sub>2</sub> (Imp.)	16	5.5	83	28			
29 SiO <sub>2</sub> -ZrO <sub>2</sub> (Imp.)	29	9.7	71	24			

[a] Number in the label is mol% SiO<sub>2</sub>. (H) - *one-pot* hydrothermal synthesis method; Imp. - Impregnation method

For the second route, monoclinic  $ZrO_2$  was *impregnated* with LUDOX TM-40 to prepare a mixed oxide enriched at the surface with SiO<sub>2</sub>. For this, monoclinic  $ZrO_2$  was prepared as shown previously <sup>[12a, 31]</sup> and LUDOX was added dropwise onto the powdered  $ZrO_2$  with various amounts as shown in **Table S6**. Subsequently, the SiO<sub>2</sub> *impregnated*  $ZrO_2$  was suspended with water, stirred for 3 h at ambient temperature and dried overnight at 110 °C. This is called *Impregnation* method (Imp.).

The 10 wt% supported Ni catalysts were prepared by the wet impregnation technique. The Ni metal precursor, Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (3.30 g) was dissolved in deionized H<sub>2</sub>O, and the resultant solution was added dropwise into 6.0 g of the powdered support with stirring in ambient air. The slurry was further stirred for 4 h, followed by drying at 110 °C overnight. Subsequently, the ground solid was calcined in synthetic air (flow rate: 100 mL·min<sup>-1</sup>) at 450 °C for 4 h (heating rate: 4 °C·min<sup>-1</sup>) and reduced in H<sub>2</sub> flow (flow rate: 100 mL·min<sup>-1</sup>) at 500 °C for 4 h (heating rate: 4 °C·min<sup>-1</sup>).

#### Catalyst characterization

**X-Ray powder diffraction (XRD)** was performed on a Philips X'Pert Pro System equipped with a Cu K $\alpha$  radiation source (40 kV/45 mA) with 1.08° min<sup>-1</sup> in the 2  $\theta$  range of 5–70°. The crystal size of ZrO<sub>2</sub> was determined *via* Scherrer equation from full width at half maximum of the (111) diffraction peak of ZrO<sub>2</sub>.<sup>[34]</sup>

**N<sub>2</sub>-sorption.** The BET surface area was determined by adsorptiondesorption with N<sub>2</sub> at -196 °C using the Sorptomatic 1990 series instrument. The sample was activated in vacuum at 250 °C for 2 h before measurement. In order to measure **H<sub>2</sub>-chemisorption** in Thermo Scientific's Surfer instrument, the Ni based catalysts were reduced in H<sub>2</sub>flow at 450 °C for 1 h and then evacuated at 300 °C for 1 h. The H<sub>2</sub> adsorption isotherms accounting for both chemisorption and physisorption were measured at a pressure ranging from 9 to 400 *m*bar at 25 °C. Afterwards, the system was evacuated for 20 min to remove physisorbed H<sub>2</sub> and to obtain chemisorbed H<sub>2</sub> after subtraction. The concentration of chemisorbed hydrogen on the metal was determined by extrapolating the isotherm to zero H<sub>2</sub> pressure. The Ni dispersion was deduced by assuming an average surface Ni to H ratio of 1.

Temperature programmed desorption (TPD) of ammonia and carbon dioxide was carried out in a 6-fold parallel reactor system. The pressed samples (500 - 710  $\mu$ m) were first activated in He at 500 °C for 1 h and loaded with the adsorbent NH<sub>3</sub> or CO<sub>2</sub> at a partial pressure of 1 *m*bar and 100 °C or 40 °C, respectively. The samples were then purged with He for 1 h in order to remove physisorbed species. After activation, the six samples were heated from 100 - 770 °C with a rate of 10 °C·min<sup>-1</sup> to desorb NH<sub>3</sub> and from 40 to 700 °C to remove CO<sub>2</sub>, and the signals were detected by a Balzers QME 200 mass spectrometer.

Atomic absorption spectroscopy (AAS) was used to determine the Ni content of the catalysts with a UNICAM 939 AA-Spectrometer. Prior to Ni determination, the catalysts were dissolved in boiling concentrated sulfuric acid. Si-content of the supports was obtained by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using a HORIBA Jobin Yvon Ultima II spectrometer. In order to prepare the sample for measurement, the finely ground powder was digested in Merck's Spectromet A14 (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, LiBO<sub>2</sub>).

**High Resolution Scanning Electron Microscopy (HR-SEM)** of the  $SiO_2$  modified supports was performed with a JOEL JSM-7500F SEM. The finely ground samples were mounted on a multi-sample-holder by standard preparation technique and measured with a secondary electron ionization detector (SEI).

IR spectroscopy of adsorbed pyridine (py-IR) was performed on a Thermo Fisher Nicolet 5700 IR spectrometer at a resolution of 4 cm<sup>-1</sup> with 120 scans in the range of 1000 - 4000 cm<sup>-1</sup> equipped with CaF<sub>2</sub> windows. For the adsorption measurements, the samples of ZrO2 with various content of SiO<sub>2</sub> were pressed into a self-supporting disc (wafer) and mounted on the sample holder. The samples were activated under vacuum ( $p = 10^{-6}$  mbar) at 450 °C for 1 h (heating ramp: 10 K·min<sup>-1</sup>). As soon as the sample cooled to 150 °C, a spectrum of the activated sample was taken. Subsequently, adsorption of pyridine was performed at 0.1 mbar for 30 min until saturation/equilibration of the surface was reached and the peak area of the IR signal remained constant. After physisorbed pyridine was removed by evacuation ( $p = 10^{-6} m bar$ ) at 150 °C, another spectrum was recorded. Finally, a spectrum was taken after desorption at 450 °C for 30 min ( $p = 10^{-6}$  mbar). The IR spectra of adsorbed pyridine were obtained by subtracting the spectrum of the activated sample, and then were normalized by the weight of the sample wafer. For quantification, the spectra were analyzed according to the procedure described earlier, using molar integral extinction coefficients of 0.73 cm·µmol<sup>-1</sup> (BAS) and 0.96 cm·µmol<sup>-1</sup> (LAS).<sup>[35]</sup>

**Solid state** <sup>29</sup>**Si MAS NMR spectroscopy measurements** (<sup>29</sup>**Si-NMR)** of SiO<sub>2</sub>-ZrO<sub>2</sub> samples were obtained using a Bruker Advance 300 MHz multinuclear FT spectrometer (B = 7.05 T) at the corresponding <sup>29</sup>Si resonance frequency of 59.6 MHz. The powdered samples were fully hydrated before packing them into a 4 mm ZrO<sub>2</sub> pencil type rotor. Spinning at a speed of 10 kHz, 7000 – 8000 scans were recorded using a single-pulse technique with a pulse length of 6 µs and a repetition time of 10 s. The external standard Si[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub> with a chemical shift of 9.8 ppm for <sup>29</sup>Si (*versus* TMS) was used.

#### Measurement of the catalytic activity

In order to test the described catalyst systems, stearic acid (0.5 g) and the corresponding catalyst (0.05 g) were first loaded into the autoclave reactor (Parr, 300 mL) with dodecane (100 mL), and then purged three times with H<sub>2</sub>. The reaction was carried out at 260 °C under 40 bar of H<sub>2</sub> for 2 h at a stirring speed of 600 rpm. *In situ* samples were drawn after 20, 40, 60, 90 and 120 min, and were analyzed by Agilent 7890B GC system,

equipped with a flame ionization detector (FID) and Agilent 5977 MS detector, using a HP-5 capillary column (30 m, 0.32 mm inner diameter, 0.25  $\mu$ m film). Reproducibility of the rates was better than ±5% for all experiments.

Conversion = (weight of converted reactant / weight of the starting reactant) × 100%. Yield (C%) = (C atoms in each product / C atoms in the starting reactant) × 100%. Selectivity (C%) = (C atoms in each product/sum of C atoms in all the products) × 100%. Turnover frequency (TOF) is the reaction rate normalized by accessible surface Ni atoms, which were determined by chemisorption of hydrogen or concentration of BAS, which was determined by *py*-IR (where applicable). TOF = mole of converted reactant / mole of accessible Ni on the catalyst's surface or mole of converted reactant / concentration of BAS. Rate of dehydration =  $\Delta$  yield of C<sub>18</sub> /  $\Delta$  time). Rate constant of dehydration = rate of dehydration / concentration of 1-octadecanol.

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**Keywords**: decarbonylation • SEM • hydrodeoxygenation • IR spectroscopy • SiO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide

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Hydrothermally synthesized  $SiO_2$ - $ZrO_2$  mixed oxide has novel nano-layers possessing Brønsted acid sites and high specific surface area. Used as supports for Ni catalyst, they enhanced the activity for fatty acid reduction compared to Ni/ZrO<sub>2</sub>.

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Controlling hydrodeoxygenation of stearic acid to *n*-heptadecane and *n*-octadecane *via* chemical properties of Ni/SiO<sub>2</sub>-ZrO<sub>2</sub>