Noble metal catalysts for the hydrodeoxyxygenation and hydrodenitrogenation of fatty amides

Emma Verkama
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Emma Verkama

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Abstract

The development of active catalysts for simultaneous hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) is important for the processing of renewable feedstocks to fuels. In this thesis, the hydrotreatment of fatty amides and their derivatives was studied on supported noble metal catalysts.

Studies on competitive HDO and HDN reactions in the co-hydrotreatment of palmitic acid and 1-tetradecylamine over Pt/ZrO₂ indicated that HDO proceeded more efficiently than HDN on all studied feed compositions. The preferential HDO of the oxygen-containing compounds and formation of secondary amides and amines via condensation reactions inhibited the HDN of 1-tetradecylamine in the co-hydrotreating experiments.

The hydrotreatment of n-hexadecanamide was studied in a batch reactor at 300 °C and 80 bar H₂, over Pt catalysts supported on SiO₂, Al₂O₃, SiO₂-Al₂O₃, TiO₂, Nb₂O₅, ZrO₂ and CeO₂-ZrO₂, as well as Pd, Rh, Ru and Ni supported on ZrO₂. The Lewis acid properties of the support influenced the activity and selectivity towards the initial n-hexadecanamide conversion route, and the conversion of the oxygen-containing intermediate products. The oxygen-containing intermediate products were converted particularly efficiently on Pt/CoO₂-ZrO₂, which was attributed to the weak Lewis acid sites on the reducible support. The active metal influenced the activity and selectivity for condensation reactions and for the formation of n-pentadecane and n-hexadecane from the intermediate products. HDO proceeded more efficiently than HDN on the studied catalysts.

Finally, monometallic and bimetallic catalysts supported on CeO₂-ZrO₂ were prepared, characterized and tested for their activity in the hydrotreatment of n-hexadecanamide. The catalytic properties of the bimetallic catalysts were markedly different compared to the corresponding monometallic catalysts, which, based on the characterization, appeared to be due to interactions between the active metals. The combination of Ni with a noble metal was particularly beneficial for the catalytic activity, and the RuNi/CoO₂-ZrO₂ catalyst exhibited the highest activity and selectivity towards the formation of n-pentadecane out of the catalysts studied in this thesis.

The results of this thesis brought new insights into the influence of the catalyst composition on the activity, selectivity and reaction network in the hydrotreatment of fatty amides to n-paraffins.

Keywords hydrotreatment, hydrodeoxygenation, hydrodenitrogenation, amide, noble metal catalyst

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Sammandrag

Utveckling av katalysatorer som är aktiva för syreavspjäckning (HDO) och kväveavspjäckning (HDN) genom vätebehandling är viktigt för att kunna omvandla förnybara råvaror till bränslen. I denna avhandling studerades aktiviteten av burna ädelmetallkatalysatorer för vätebehandling av alifatiska amidar.

Studier om tävlande HDO och HDN reaktioner i vätebehandlingen av palmitinsyra och 1-tetradekylamin på en Pt/ZrO₂ katalysator indikerade att HDO framskriver effektivare än HDN. Detta gällde för alla studerade reaktantkompositioner. HDN av 1-tetradekylamin inhiberades av HDO av de mer reaktiva syrehaltiga föreningarna, samt av bildningen av sekundära amidor och aminer genom kondensationsreaktioner.

Aktiviteten av Pt katalysatorer burna av SiO₂, Al₂O₃, SiO₂-Al₂O₃, TiO₂, Nb₂O₅, ZrO₂ och CeO₂-ZrO₂, samt Pd, Rh, Ru och Ni katalysatorer burna av ZrO₂, studerades i vätebehandlingen av n-hexadekanamid i en satsreaktor (300 °C och 80 bar H₂). Bärraras Lewis-syra egenskaper påverkade aktiviteten och selektiviteten både för den primära reaktionsvägen för n-hexadekanamin, och för konversionen av de syrehaltiga mellanprodukterna. De syrehaltiga mellanprodukterna omvandlades effektivt på Pt/CeO₂-ZrO₂, vilket var på grund av de svaga Lewis-syrasäten på den reducerbara bärraren. Den aktiva metallen påverkade aktiviteten och selektiviteten för kondensationsreaktioner och för bildningen av n-pentadekan och n-hexadekan från mellanprodukterna. Alla katalysatorer uppfannade en högre aktivitet för syreavspjäckning än kväveavspjäckning.

Slutligen syntetiserades och karakteriserades en serie monometalliska och bimetalliska katalysatorer på en CeO₂-ZrO₂ bärra. De bimetalliska katalysatorernas aktivitet i vätebehandlingen av n-hexadekanamid avveck märkbart från de monometalliska katalysatorerna, vilket på basis av karakteriseringsdatan verkade vara på grund av växelverkan mellan de aktiva metallerna. Kombinationen av nickel med en ädelmetall visade sig vara effektiv, och RuNi/CeO₂-ZrO₂ åstadkom den högsta aktiviteten och selektiviteten för bildningen av n-pentadekan av alla katalysatorer som utvärderades i denna avhandling.

Resultaten av denna avhandling gav ny information om katalysatorkombinationens inverkan på aktiviteten, selektiviteten och reaktionsnätverket i vätebehandlingen av alifatiska amidor till n-alkaner.

Nyckelord katalytisk vätebehandling, kväveavspjäckning, syreavspjäckning, amid, ädelmetallkatalysator

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Freiburg im Breisgau, 16th of March 2024
Emma Verkama
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List of Abbreviations and Symbols

**Abbreviations**

a.u.  
arbitrary unit

BAS  
Bronsted acid site

BDA  
bimolecular deammoniation

BET  
Brunauer-Emmett-Teller

BJH  
Barrett-Joyner-Halenda

C14 alcohol  
1-tetradecanol

C14 amine  
1-tetradecylamine

C14 paraffin  
n-tetradecane

C15 paraffin  
n-pentadecane

C16 acid  
palmitic acid (hexadecanoic acid)

C16 alcohol  
1-hexadecanol

C16 aldehyde  
n-hexadecanal

C16 amide  
n-hexadecanamide

C16 amine  
1-hexadecylamine

C16 nitrile  
n-hexadecanitrile

C16 paraffin  
n-hexadecane

C17 amine  
isopropyl tetradecylamine

C17 ester  
methyl palmitate

C28 amine  
n-tetradecyl tetradecylamine

C30 amide  
n-tetradecyl hexadecanamide

C30 amine  
n-tetradecyl hexadecylamine

C31 ketone  
dipentadecylketone

C32 amide  
n-hexadecyl hexadecanamide
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C32 amine</td>
<td>n-hexadecyl hexadecylamine</td>
</tr>
<tr>
<td>C32 ester</td>
<td>palmityl palmitate (hexadecyl hexadecanoate)</td>
</tr>
<tr>
<td>C&lt;sub&gt;n&lt;/sub&gt;</td>
<td>molecule with &lt;i&gt;n&lt;/i&gt; carbon atoms in the carbon chain</td>
</tr>
<tr>
<td>COND</td>
<td>condensation</td>
</tr>
<tr>
<td>deHYD</td>
<td>dehydrogenation</td>
</tr>
<tr>
<td>DHY</td>
<td>dehydration</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionization detector</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared (spectroscopy)</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HDN</td>
<td>hydrodenitrogenation</td>
</tr>
<tr>
<td>HDO</td>
<td>hydrodeoxygenation</td>
</tr>
<tr>
<td>HDS</td>
<td>hydrodesulfurization</td>
</tr>
<tr>
<td>HTL</td>
<td>hydrothermal liquefaction</td>
</tr>
<tr>
<td>HYD</td>
<td>hydrogenation</td>
</tr>
<tr>
<td>HYDR</td>
<td>hydrolysis</td>
</tr>
<tr>
<td>IWI</td>
<td>incipient wetness impregnation</td>
</tr>
<tr>
<td>KET</td>
<td>bimolecular ketonization</td>
</tr>
<tr>
<td>LAS</td>
<td>Lewis acid site</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometer</td>
</tr>
<tr>
<td>n.a.</td>
<td>not applicable</td>
</tr>
<tr>
<td>NPD</td>
<td>nitrogen phosphorus detector</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TMS</td>
<td>transition metal sulfide</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature programmed desorption</td>
</tr>
<tr>
<td>TPR</td>
<td>temperature programmed reduction</td>
</tr>
<tr>
<td>VacI</td>
<td>vacuum impregnation</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
XRD  X-ray diffraction  
XRF  X-ray fluorescence  

**Symbols**

\( \tau \)  
batch residence time \((g_{\text{cat}}/h)/g_{\text{reactant}}\)

\( \mu_i \)  
stoichiometric factor for product \( i \) (-)

\( B_C \)  
carbon balance closure (mol %)

\( d_{\text{particle}} \)  
mean metal particle size (nm)

\( d_{p, \text{mean}} \)  
mean pore diameter (nm)

\( c_i \)  
molar share of compound \( i \) in the reaction products (mol %)

\( c_{\text{N, feed}} \)  
nitrogen content of the feed mixture (ppm)

\( c_{\text{N, products}} \)  
nitrogen content of the reaction products (ppm)

\( c_{\text{O, feed}} \)  
oxygen content of the feed mixture (ppm)

\( c_{\text{O, products}} \)  
oxygen content of the reaction products (ppm)

\( D \)  
metal dispersion (%)

\( m \)  
mass (g)

\( m_{\text{cat}} \)  
mass of the catalyst (g)

\( m_{A,0} \)  
mass of the reactant (g)

\( n \)  
amount of substance (mol)

\( n_{\text{C14 amine+ C16 acid},0} \)  
total amount of C14 amine and C16 acid in the reaction mixture (mol)

\( n_{i,0} \)  
amount of compound or element \( i \) in the feed mixture (mol)

\( n_i \)  
amount of compound or element \( i \) in the reaction products (mol)

\( P \)  
pressure (bar)

\( S_{\text{BET}} \)  
specific surface area (m²/g)

\( t \)  
reaction time (h)

\( T \)  
temperature (°C)

\( V_{\text{pore}} \)  
specific pore volume (cm³/g)

\( x_i \)  
molar fraction of compound \( i \) (%)

\( X_A \)  
conversion of reactant \( A \) (%)
$Y_i$  
yield of compound $i$ (%)
List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

I. Verkama, Emma; Auvinen, Paavo; Albersberger, Sylvia; Tiitta, Marja; Karinen, Reetta; Puurunen, Riikka L. 2023. Competitive hydrodeoxygenation and hydrodenitrogenation reactions in the hydrotreatment of fatty acid and amine mixtures. Topics in Catalysis, volume 66, pages 1353-1368. https://doi.org/10.1007/s11244-023-01784-w


III. Verkama, Emma; Albersberger, Sylvia; Meinander, Kristoffer; Tiitta, Marja; Karinen, Reetta; Puurunen, Riikka L. 2024. Zirconia-supported Pt, Pd, Rh, Ru and Ni catalysts in the hydrotreatment of fatty amides and amines. Energy & Fuels, volume 38, pages 4464-4479. https://doi.org/10.1021/acs.energyfuels.3c04372

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**Author’s Contribution**

**Publication I:** Competitive hydrodeoxygenation and hydrodenitrogenation reactions in the hydrotreatment of fatty acid and amine mixtures

E.V. prepared the catalyst, carried out the batch reactor experiments and analyzed the reaction products. P.A. performed a part of the GC-MS analysis. The experiments were planned by E.V., R.K., S.A., M.T. and R.L.P. E.V. wrote the first version of the manuscript. All authors contributed to the final version of the manuscript.

**Publication II:** Hydrodeoxygenation and hydrodenitrogenation of n-hexadecanamide over Pt catalysts: effect of the support

E.V. prepared the catalysts, carried out all catalyst characterization except for the XPS and STEM measurements, performed most activity tests and analyzed the reaction products. K.M. carried out the XPS measurements. A.A. participated in the selection of the model compound and the solvent, and in the initial activity tests. The analytics were developed by E.V. and A.A. The experiments were planned by E.V., A.A., S.A., R.K., M.T. and R.L.P. The first version of the manuscript was written by E.V. All authors contributed to the final version of the manuscript.

**Publication III:** Zirconia-supported Pt, Pd, Rh, Ru and Ni catalysts in the hydrotreatment of fatty amides and amines

E.V. prepared the catalysts, carried out all catalyst characterization except for the XPS and STEM measurements, performed most of the activity tests and analyzed the reaction products. E.V. planned the experiments in collaboration with S.A., R.K., M.T. and R.L.P. K.M. carried out the XPS measurements. E.V. wrote the first version of the manuscript. All authors contributed to the final version of the manuscript.

**Publication IV:** Hydrodeoxygenation and hydrodenitrogenation of n-hexadecanamide to n-paraffins: bimetallic catalysts supported on ceria-zirconia

E.V. prepared the catalysts, carried out all catalyst characterization except for the XPS and STEM measurements. The catalytic activity tests were performed by E.J. and E.V. The experimental plan was created by E.V., in collaboration with S.A., M.T., R.K. and R.L.P. The XPS measurements
were performed by K.M and the STEM images were taken by H.J. E.V. wrote the first version of the manuscript. All authors contributed to the final version of the manuscript.
1. Introduction

The global CO₂ emissions need to be decreased to mitigate global warming. The Renewable Energy Directive of the European Union (EU) requires 32% of the total energy consumed in the EU to be renewable by 2030.¹ The directive, which has been effective since December 2018, further outlines that the share of biofuels in the transport sector must be increased to at least 14% by 2030.¹ Since its introduction, the Renewable Energy Directive has been revised, and a provisional agreement to increase the overall share of renewable energy to a minimum of 42.5% was reached in 2023.²

To meet the climate and renewable energy targets, the global demand for renewable fuels has been projected to rise significantly on a yearly basis, as illustrated in Figure 1.³ In Figure 1, biodiesel refers to fatty acid methyl esters, whereas renewable diesel refers to hydrotreated vegetable oils. Renewable transport fuels with a high energy density are essential to sustainably power existing fleet, as well as the heavy-duty transport sector and aviation industry, where the current battery technologies do not accommodate for large-scale electrification.⁴⁵

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Projected growth in biofuel demand per year for advanced and emerging economies (2022-2027). Adapted from Ref. 3 (licensed under CC BY 4.0).
1.1 Renewable transport fuels

Biofuels can be produced via several technologies, which can be differentiated based on the origin of the feedstock and the technological maturity.\textsuperscript{5,6} Conventional 1\textsuperscript{st} generation biofuels are produced from edible crops, while 2\textsuperscript{nd} generation biofuels use feedstocks that do not compete with the food production, such as lignocellulosic biomass, inedible plant oils, wastes and residues.\textsuperscript{5,6} Bioethanol obtained via the fermentation of corn or sugarcane and biodiesel produced via the transesterification of vegetable oils are examples of 1\textsuperscript{st} generation biofuels. Cellulosic ethanol and renewable diesel obtained via the hydrotreatment of waste fats are examples of 2\textsuperscript{nd} generation biofuels.\textsuperscript{5,6} Algae-originating fuels are often classified as 3\textsuperscript{rd} generation biofuels.\textsuperscript{5,6}

Hydrotreating is a viable strategy for the production of fuels and chemicals from biobased feedstocks of diverse origins.\textsuperscript{6–10} In hydrotreating processes, a feedstock is contacted with hydrogen in the presence of a catalyst under an elevated temperature and pressure.\textsuperscript{11–13} Hydrotreating reactions include, but are not limited to, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), hydrocracking, and hydrogenation of unsaturated and aromatic structures.\textsuperscript{11–13} The relative importance of these reactions depends on the feedstock, reaction conditions and the used catalyst.\textsuperscript{11–13}

The oxygen content of biobased feedstocks and biocrudes can be close to 50\%.\textsuperscript{13,14} The oxygen content must be decreased in order to meet fuel specifications, as oxygen-containing compounds are reactive, corrosive, increase the viscosity and lower the heating value.\textsuperscript{15,16} HDO reactions are therefore of particular importance in the upgrading of biobased feedstocks and biocrudes to fuels. Significant research efforts have, indeed, been devoted to the HDO of various plant oils and biocrudes to fuels in the past decades.\textsuperscript{7,8,15,17,18}

Some biobased feedstocks, e.g., animal fats and biocrudes obtained via the hydrothermal liquefaction (HTL) of algae and sewage sludge, contain nitrogen in addition to oxygen.\textsuperscript{19–23} The nitrogen content of tallow can range from approximately 100 and 1300 ppm\textsuperscript{20}, while HTL biocrudes can contain between 5 and 10 wt. \% nitrogen.\textsuperscript{21,22,24,25} The nitrogen-containing fraction comprises, e.g., fatty amides, amines, indole, pyrroles and other heterocyclic aromatic compounds.\textsuperscript{19–23} In studies on the upgrading of HTL biocrudes to fuels via hydrotreating, almost complete oxygen removals have been achieved, while nitrogen removal levels typically only range between 50 and 80\%.\textsuperscript{9,22,26,27}

Nitrogen-containing compounds have a negative impact on the fuel stability and poison catalysts in downstream processing units.\textsuperscript{12} The nitrogen content of renewable feedstocks must therefore be decreased in parallel with the oxygen content, which makes the development of catalysts which are active for both HDO and HDN important. For the purpose of catalyst development, the use of representative model compounds instead of complex real feeds can be desirable, as they enable achieving a deeper understanding of the reaction network and the reaction mechanisms.\textsuperscript{28} Primary fatty amides, such as tetradecanamide (C\textsubscript{14}H\textsubscript{29}NO), hexadecanamide (C\textsubscript{16}H\textsubscript{33}NO), octadecanamide (C\textsubscript{18}H\textsubscript{37}NO) and oleamide (C\textsubscript{18}H\textsubscript{35}NO), are relevant model compounds for studying simultaneous HDN and HDO of renewable feedstocks, due to their prevalence in both HTL
biocrudes and animal fats.\textsuperscript{19–23} The knowledge on the HDO and HDN of primary amides to paraffins is, however, limited.\textsuperscript{29}

1.2 Hydrotreating catalysts

Sulfided Mo (or W) catalysts, promoted by Ni or Co and supported on, e.g., Al$_2$O$_3$ or SiO$_2$-Al$_2$O$_3$, are commercially used for the hydrotreatment of fossil and renewable feedstocks.\textsuperscript{12} The active sites of transition metal sulfide (TMS) catalysts are sulfur vacancies (coordinatively unsaturated sites) at the edges of the Mo(W)S$_2$ slabs, and Brønsted acidic sulphydryl (SH) groups.\textsuperscript{12} The currently most accepted model for the structural incorporation and promotional effect of Co and Ni is the Co(Ni)-Mo-S structure proposed by Topsøe et al.\textsuperscript{30,31} Both Ni and Co can donate electrons to Mo, which weakens the metal-sulfur bond and increases the catalytic activity.\textsuperscript{32,33}

Sulfided CoMo catalysts exhibit a higher activity for HDS than sulfided NiMo catalysts.\textsuperscript{34} Meanwhile, NiMo-based catalysts show a higher hydrogenation activity than CoMo, and are thus well suited for HDN.\textsuperscript{34} The enhanced hydrogenation activity of NiMo can be attributed to the location of the Ni and Co cations, with Co located at the S edge, and Ni at the metal edge.\textsuperscript{34} The hydrogenation activity of sulfided NiW catalysts further exceeds the hydrogenation activity of NiMo.\textsuperscript{34}

It should be noted, that TMS catalysts need to remain sulfided to maintain their activity.\textsuperscript{33} A sulfur source must therefore be added to the feed when TMS catalysts are used for the hydrotreatment of renewable, sulfur-free feedstocks.\textsuperscript{13} This leads to sulfur-contamination of the product, and imposes a need for a purification step.\textsuperscript{35}

Supported noble metal catalysts provide an alternative to TMS catalysts for the hydrotreatment of renewable, sulfur free feedstocks. Supported noble metals, such as Pt, Pd, Ru, Rh, Ir and Os, are active in their reduced state and are capable of activating hydrogen in relatively mild conditions.\textsuperscript{36} The activity and selectivity of noble metal catalysts depend both on the active metal and the used support.\textsuperscript{17,35-37,38} The support can introduce Lewis acid and basic sites, Brønsted acid sites, redox sites and/or oxophilic sites to the system, which influence the adsorption of the reactant and favored reaction pathway(s).\textsuperscript{35,37,39,40} The widely used γ-Al$_2$O$_3$ is an example of a Lewis acidic oxide, while SiO$_2$-Al$_2$O$_3$ materials and zeolites additionally contain Brønsted acid sites.\textsuperscript{41,42} TiO$_2$ and CeO$_2$-ZrO$_2$ are examples of reducible and oxophilic supports.\textsuperscript{43-47} Not only the nature of the active phase, but also the reaction mechanisms differ between reduced noble metal and TMS catalysts.\textsuperscript{12,48}

The activity of noble metal catalysts can exceed the activity of TMS catalysts, particularly in hydrogenation and hydrodeoxygenation reactions. Milder operation conditions, e.g., 100-350 °C and 1-50 bar H$_2$ can thus be used for noble metal catalysts, than what typically are used for TMS catalysts, 250-400 °C and 10-100 bar H$_2$.\textsuperscript{34,36} However, noble metal catalysts are expensive, and in contrast to TMS catalysts, prone to deactivation by sulfur poisoning, which limits their applicability for the hydrotreatment of sulfur-containing
feedstocks. Improvements in the sulfur tolerance and coking resistance of noble metal catalysts have been demonstrated by alloying noble metals with base metals or other noble metals. Bimetallic catalysts which contain a noble metal and a base metal, e.g., RuNi and PtNi, have also been reported to exhibit a higher activity in HDO reactions compared to their monometallic counterparts. Combining a noble metal with a base metal may thus improve the stability and can enable decreasing the noble metal loading and the price of the catalyst, without compromising the activity.

1.3 Scope of this research

In this dissertation, the HDO and HDN of fatty amides and their derivatives was studied on supported noble metal catalysts. The purpose of this work is to gain new insights into the amide hydrotreating reaction network and on the influence of the catalyst composition on the activity and selectivity. The key aims of this thesis can be summarized as follows:

- Understanding competitive HDO and HDN reactions on supported noble metal catalysts and investigating the relative reactivity of oxygen-containing and nitrogen-containing compounds [I]. This study was carried out by co-hydrotreating a fatty acid and an alkyl amine, as it enabled varying the oxygen and nitrogen content independent of each other and allowed following the formation of n-paraffins from each model compound accurately.
- Formulating a reaction network for the HDO and HDN of fatty amides to n-paraffins on supported noble metal catalysts [I-III].
- Understanding the impact of the catalyst support [II] and active metal [III] on the activity and selectivity for the hydrotreatment of amides, by correlating the characterized properties with the activity test data.
- The development of active of active and selective bimetallic catalysts for the hydrotreatment of amides to n-paraffins, based on the studies of the reaction network and the influence of the catalyst composition [IV].

Accordingly, the focus areas of this thesis are visualized in Figure 2.
2. Noble metal catalysts for hydrotreating

This chapter provides information on the activity of noble metal catalysts in reactions that are relevant for the hydrotreatment of fatty amides to paraffins. The hydrogenation of amides to amines and alcohols is discussed in Section 2.1. Sections 2.2 and 2.3 provide an overview on the activity of supported noble metal catalysts in the HDO of fatty acids and alcohols, and in the HDN of amines, respectively.

2.1 Hydrogenation of amides

While published research on the HDO and HDN of amides to paraffins is limited,21,29 studies on the hydrogenation of amides to alcohols and amines has been carried out both on homogeneous and heterogeneous catalysts.59–74 Particularly the production of structurally complex amines via the C–O bond hydrogenolysis of amides has attracted interest, due to the importance of amines in the pharmaceutical and agrochemical industries.62,67 The carbonyl group of amides is only weakly electrophilic due to delocalization of the lone electron pair of the nitrogen, which renders the hydrogenation of amides challenging.62,67 The control over the selectivity for the C–N and C–O bond cleavage pathways, and the formation of undesirable secondary diamines, are further challenges, particularly in the case of primary amides.62,67,73

A simplified reaction network for the hydrogenation of a secondary amide is presented in Figure 3, while Table 1 gives an overview on amide hydrogenation studies that have been carried out over heterogeneous noble metal catalysts. Only the details of the most active catalyst and the main model compound the study focused on are presented in the table, in cases where the studies comprised several catalysts or included multiple model compounds. The next sections highlight some of the key findings from the studies.
Figure 3. Simplified reaction network for the hydrogenation of a secondary amide. The hydrogenation of primary and tertiary amides proceeds analogously. Hydrogenation is abbreviated as HYD. The reaction network has been compiled from the reaction pathways presented in Refs. 61, 62, 68, 72 and 73.

Table 1. Examples on amide hydrogenation studies

<table>
<thead>
<tr>
<th>Model compound</th>
<th>Amide type</th>
<th>Desired cleavage pathway</th>
<th>Catalyst</th>
<th>Conversion, yield, selectivity</th>
<th>Reaction conditions</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanamide + others</td>
<td>Primary (+ secondary, tertiary)</td>
<td>C–O</td>
<td>Ru-WO\textsubscript{9}/MgAl\textsubscript{2}O\textsubscript{4} (+other metals and supports)</td>
<td>X = 100% Y = 83%</td>
<td>200 °C, 50 bar H\textsubscript{2}, 6 bar NH\textsubscript{3}, 7 h</td>
<td>Coeck et al.\textsuperscript{73}</td>
</tr>
<tr>
<td>Cyclohexanecarboxamide + others</td>
<td>Primary (+ secondary, tertiary)</td>
<td>C–O</td>
<td>Ru-WO\textsubscript{9}/SiO\textsubscript{2} (several ratios of Ru and W)</td>
<td>X = 94% S = 84%</td>
<td>160 °C, 50 bar H\textsubscript{2}, 12 h</td>
<td>Zhang et al.\textsuperscript{67}</td>
</tr>
<tr>
<td>Cyclohexanecarboxamide</td>
<td>Primary (+ tertiary)</td>
<td>C–O</td>
<td>Rh-MO\textsubscript{9}/SiO\textsubscript{2} (+ other metals)</td>
<td>X = 74% S = 43%</td>
<td>140 °C, 80 bar H\textsubscript{2}, 24 h</td>
<td>Nakagawa et al.\textsuperscript{61}</td>
</tr>
<tr>
<td>Cyclohexanecarboxamide + others</td>
<td>Primary (+ tertiary)</td>
<td>C–O</td>
<td>Rh/Mo (+ others)</td>
<td>X = 100% S = 87%</td>
<td>160 °C, 100 bar H\textsubscript{2}, 16 h</td>
<td>Beamson et al.\textsuperscript{68}</td>
</tr>
<tr>
<td>Cyclohexanecarboxamide + others</td>
<td>Primary (+ secondary, tertiary)</td>
<td>C–O</td>
<td>Ru/Mo (+ others)</td>
<td>X = 100% S = 85%</td>
<td>160 °C, 100 bar H\textsubscript{2}, 16 h</td>
<td>Beamson et al.\textsuperscript{69}</td>
</tr>
<tr>
<td>Cyclohexanecarboxamide + others</td>
<td>Primary (+ tertiary)</td>
<td>C–O</td>
<td>Ru/Re (+ others)</td>
<td>X = 100% S = 93%</td>
<td>160 °C, 100 bar H\textsubscript{2}, 16 h</td>
<td>Beamson et al.\textsuperscript{70}</td>
</tr>
<tr>
<td>n-acetylpiperidin-2-one + others</td>
<td>Tertiary (+ secondary)</td>
<td>C–O</td>
<td>Pt/Nb\textsubscript{2}O\textsubscript{5} (+ other metals and supports)</td>
<td>X = 100% Y = 99%</td>
<td>160-200 °C, 50 bar H\textsubscript{2}, 24 h</td>
<td>Shimizu et al.\textsuperscript{59}</td>
</tr>
<tr>
<td>n-acetylpiperidine</td>
<td>Tertiary</td>
<td>C–O</td>
<td>Rh/C + Re/C (+ other metals, inc. metal carbonyls)</td>
<td>X = 100% S = 98%</td>
<td>170 °C, 100 bar H\textsubscript{2}, 16 h</td>
<td>Hirosawa et al.\textsuperscript{74}</td>
</tr>
<tr>
<td>n-methylpyrrolidin-2-one</td>
<td>Tertiary</td>
<td>C–O</td>
<td>Pt-Re/TiO\textsubscript{2} (+ other metals and supports)</td>
<td>X &gt; 90% S = 100%</td>
<td>120 °C, 20 bar H\textsubscript{2}, 24 h</td>
<td>Burch et al.\textsuperscript{60}</td>
</tr>
<tr>
<td>Cyclohexanecarboxamide + others</td>
<td>Primary (+ secondary, tertiary)</td>
<td>C–N</td>
<td>Ru/ReO\textsubscript{2} (+ other metals and supports)</td>
<td>X = 52% S = 97%</td>
<td>60 °C, 80 bar H\textsubscript{2}, 4 h water</td>
<td>Tamura et al.\textsuperscript{71}</td>
</tr>
<tr>
<td>Benzaniilde + others</td>
<td>Secondary (+ primary, tertiary)</td>
<td>C–N</td>
<td>Ag/γ Al\textsubscript{2}O\textsubscript{3} (+ other supports)</td>
<td>X = 75% Y = 73%</td>
<td>150 °C, 50 bar H\textsubscript{2}, 24 h, 10% (CH\textsubscript{3})\textsubscript{2}CO\textsubscript{K}</td>
<td>Xie et al.\textsuperscript{69}</td>
</tr>
</tbody>
</table>
Zhang et al.\textsuperscript{67} evaluated the activity of bifunctional Ru-W/SiO\textsubscript{2} catalysts in the hydrogenation of cyclohexanecarboxamide at 160 °C and 50 bar H\textsubscript{2}. Oxophilic W\textsuperscript{5+} sites at the Ru-W interface were suggested to activate the C=O bond, which facilitated the selective HDO of the amide to the amine.\textsuperscript{67} The proposal was based on diffuse reflectance infrared Fourier transform infrared spectroscopy (DRIFTS) studies on the adsorption of acetamide on the catalysts.\textsuperscript{67} The DRIFTS studies indicated that the monometallic Ru catalyst could activate both the C=O and C–N bonds, explaining the formation of both the amine and the undesirable alcohol on the monometallic Ru catalyst.\textsuperscript{67} The reaction mechanism was proposed to proceed analogously to the mechanism in Figure 3, with the initial formation of a hemiaminal type intermediate.\textsuperscript{67} The hemiaminal, in turn, decomposed to an imine (or aldehyde), which in turn was hydrogenated to the amine (or alcohol) over the Ru sites.\textsuperscript{67} The formation of an unstable hemiaminal intermediate has been proposed by multiple other authors, and is likely the rate limiting step in the hydrogenation of amides.\textsuperscript{61,62,68,72,73} In addition to the pathways presented in Figure 3, it should be noted that the oxygen removal of primary amides can proceed via the dehydration to a nitrile.\textsuperscript{62,75,76,70} Shimizu et al.\textsuperscript{59} investigated the selective hydrogenation of n-acetylpiperidine to the corresponding amine over a series of supported noble metal catalysts. Pt/Nb\textsubscript{2}O\textsubscript{5} exhibited the highest activity, which the authors attributed to Lewis acid-base interaction between the Lewis acid sites of the partially reduced Nb\textsubscript{2}O\textsubscript{5} support and the carbonyl group of the amide.\textsuperscript{59} The reaction was suggested to proceed via the adsorption and activation of the amide carbonyl group on the Lewis acid sites of partially reduced support species at the perimeter of the Pt particles, and hydrogenation catalyzed by Pt.\textsuperscript{59} A similar mechanism was proposed by Burch et al.\textsuperscript{60} for the hydrogenation of n-methylpyrrolidin-2-one on bimetallic Pt-Re/TiO\textsubscript{2} catalysts, with Re activating the carbonyl group and Pt hydrogenating the intermediates. It thus appears, that Lewis acid activation of the amide carbonyl group is beneficial for the catalytic activity in the hydrogenation of amides.

The addition of ammonia can increase the amine selectivity by promoting the amination of alcohols and suppressing the formation of secondary amines, but typically also results in a decreased reaction rate.\textsuperscript{59,73} For example, Coeck et al.\textsuperscript{73} achieved a 84% hexylamine selectivity at ~90% conversion, in the hydrogenation of hexanamide on Ru-WO\textsubscript{4}/SiO\textsubscript{2} at 200 °C, 50 bar H\textsubscript{2}, a reaction time of 7 h and 6 bar NH\textsubscript{3}. Without the addition of NH\textsubscript{3}, a complete hexanamide conversion was obtained already after 2 h, but the hexylamine selectivity was less than 25%.\textsuperscript{73} The highest hexylamine yield at full conversion, 83%, was obtained on a Ru-WO\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4} catalyst.\textsuperscript{73}

As can be observed from Table 1, the studies on the C–O cleavage of amides vastly outnumber the studies on the C–N bond cleavage of amides. Xie et al.\textsuperscript{72} used a strong base in the reaction medium to facilitate the C–N cleavage of benzanilide. Tamura et al.\textsuperscript{71} obtained a 97% selectivity towards the C–N bond cleavage of cyclohexanecarboxamide on a Ru/CeO\textsubscript{2} catalyst, using water as a solvent.\textsuperscript{77} Water can promote the C–N bond cleavage of the amide via hydrolysis to a carboxylic acid.\textsuperscript{71}
2.2 Hydrodeoxygenation of fatty acids and alcohols

Fatty acids and alcohols can be formed as intermediate products in the hydrotreatment of amides. The activity of supported Pt, Pd, Ru, Rh and Ni catalysts has widely been demonstrated in the HDO of fatty acids. Figure 4 shows a simplified reaction network for the HDO of fatty acids on reduced metal catalysts. The reaction network has been compiled from the reaction pathways presented in Refs. 37,38,43 and 85.

Decarboxylation, decarbonylation, and HDO via C–O bond hydrolysis are the three main oxygen removal routes in the hydrotreatment of fatty acids, as shown in Figure 4. The decarboxylation of a C_n fatty acid yields the C_{n-1} paraffin and CO_2. The decarbonylation of a C_n fatty acid likewise gives the C_{n-1} paraffin, but involves a primary hydrogenolysis step to the C_n aldehyde, out of which the oxygen is cleaved as CO. Both the decarboxylation of a C_n fatty acid and the decarbonylation of the C_n aldehyde are catalyzed by the metal sites. The decarbonylation and decarboxylation routes tend to dominate on noble metal catalysts, particularly...
when neutral supports are used.\textsuperscript{37,38,77–83} This is a key difference to TMS catalysts, which generally favor C–O bond hydrogenolysis.\textsuperscript{37,84,86,87}

In contrast to decarbonylation and decarboxylation routes, the C–O bond hydrogenolysis of C\(_n\) fatty acids yields the C\(_n\) paraffin (Figure 4). The reaction proceeds via a sequence of hydrogenation and dehydration steps, involving the intermediate formation of the C\(_n\) aldehyde and the C\(_n\) alcohol, with the oxygen cleaved as H\(_2\)O\textsuperscript{37,86}

The HDO of C\(_n\) fatty alcohols can proceed via the hydrogenolysis (or direct deoxygenation) to the C\(_n\) paraffin\textsuperscript{37,86} The C\(_n\) paraffin can alternatively be obtained via the dehydration of the C\(_n\) alcohol to a C\(_n\) olefin, and subsequent hydrogenation of the C\(_n\) olefin to the C\(_n\) paraffin\textsuperscript{37,86} The dehydrogenation of the C\(_n\) alcohol to the C\(_n\) aldehyde and subsequent decarbonylation to the C\(_{n-1}\) paraffin can also occur\textsuperscript{85,88}.

The HDO of fatty acids and alcohols via C–O bond hydrogenolysis has been proposed to occur via different bifunctional mechanisms, which involve both metal sites and Lewis or Brønsted acid sites of the support.\textsuperscript{37,81,89} Here, the role of the active metal is to hydrogenate the intermediate products.\textsuperscript{37,81,89} The Lewis acid sites of the support promote the adsorption of the reactants and activate carbonyl groups, while Brønsted acid sites bring activity for the dehydration of alcohols.\textsuperscript{37,81,89} Lewis acidic and reducible supports exhibit activity for the conversion of fatty acids to aldehydes even without the presence of an active metal, via a reverse Mars–van–Krevelen type mechanism.\textsuperscript{85,90,91}

Noble metal catalysts that are supported by reducible oxides (e.g., TiO\(_2\), Nb\(_2\)O\(_5\) and CeO\(_2\)-ZrO\(_2\)) are capable of activating carbonyl groups at mild temperatures, and can show a superior HDO activity compared to noble metal catalysts on irreducible supports.\textsuperscript{37,43,87} The enhancing effect of reducible and oxophilic supports has also been established in the HDO of other oxygenates, such as phenolics.\textsuperscript{40,92–95}

The fatty acid HDO pathways differ in terms of H\(_2\) consumption, with the C–O hydrogenolysis consuming the most hydrogen.\textsuperscript{37,86} No net H\(_2\) consumption is associated with the decarboxylation of fatty acids.\textsuperscript{37,86} In practice, the H\(_2\) consumption is also affected by the extent of which gas phase reactions, such as the reverse water gas shift and methanation, occur.\textsuperscript{84,85}

Heavy C\(_{2n}\) esters can be formed as intermediate products in the hydrotreatment of fatty acids on reduced metal catalysts (Figure 4).\textsuperscript{39,43} The esters can be hydrolyzed back to the C\(_n\) acid and the C\(_n\) alcohol, or undergo hydrogenolysis to the C\(_n\) aldehyde and C\(_n\) alcohol, which proceed to be converted to paraffins as described previously.\textsuperscript{39,43}

2.3 Hydrodenitrogenation of amines

As established in Section 2.1, amines are readily formed in the hydrogenation of amides. Reduced metals are known to exhibit activity for the C–N bond hydrogenolysis of amines, but HDN studies of amines (and other nitrogen-containing molecules) are considerably more scarce than HDO studies.\textsuperscript{48,96–100} Figure 5 presents a simplified reaction network for the HDN of alkyl amines on
Noble metal catalysts for hydrotreating

reduced metal catalysts. The reaction network has been compiled from the reaction pathways presented in Refs. 48,96 and 101.

Figure 5. Simplified reaction network for the HDN of a primary alkylamine on reduced metal catalysts. The reaction network has been compiled from the reaction pathways presented in Refs. 48,96 and 101.

The metal catalyzed C–N hydrogenolysis of methylamine to methane has been studied both computationally and experimentally. The mechanism is initiated by the dissociative adsorption of methylamine as a hydrogen deficient surface species, CH₃NH₂. Each amine occupies two metal sites, one bonding with the α-carbon and one with the amine group. The metal identity influences both the adsorption mode and the transition state. For example, the initial hydrogen cleavage channel and the number of hydrogen atoms that are cleaved from the adsorbed amine species before the C–N hydrogenolysis occurs can be affected.

According to the computational methylamine HDN study by Almithn and Hibbitts, the group 8-11 transition metals (Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au) all cleave two hydrogen atoms from the carbon, before C–N hydrogenolysis occurs (CH₃ → CH). Meanwhile, the number of hydrogen atoms cleaved from the amine group varies from zero to two, depending on the active metal (NH₂ → N, NH or NHₓ). Ru and Os cleave both hydrogen atoms from the amine group, while the metals of the groups 9-11 only partially dehydrogenate the amine group prior to the C–N bond cleavage. Experimental and computational studies agree that the C–N cleavage is the rate limiting step in the HDN of methylamine, and that the activity of the transition metals of the groups 8-11 decreases from left to right in the periodic table.

The mechanism for the HDN of methylamine can be transposed to longer chain alkylamines, as demonstrated by Cattenot et al. It should, however, be noted that a competition between C–C and C–N bond cleavage pathways may occur in the hydrotreatment of amines with longer carbon chains, and that steric
factors can influence the adsorption.\(^{88,100}\) The C–C bond cleavage of amines has only been reported rarely\(^{88}\), and the mechanism is not completely understood.

The HDN of alkyl amines can also proceed via Brønsted acid catalyzed Hofmann elimination to an olefin (Figure 5).\(^{105}\) The hydrogenation of the olefin to a paraffin proceeds on the metal sites.\(^{101}\)

The formation of secondary amines via the disproportionation of primary amines occurs in parallel with HDN on reduced metals (Figure 5).\(^{48,96–99}\) The secondary amines can be converted to paraffins, or undergo further condensation reactions with primary amines and form tertiary amines.\(^{48,96,101}\)

The selectivity between HDN and disproportionation strongly depends on the active metal. For example, Rh strongly favors the formation of hydrocarbons, while the formation of secondary and tertiary amines dominates on Pd.\(^{48,96–99}\)

Differences in the adsorption mode and adsorption strength, as observed in the methylamine HDN studies,\(^{96–98,100,102–104}\) may explain the selectivity differences between the metals.

According to Sivasankar and Prins\(^{101}\), the decomposition of secondary amines can occur via elimination, which yields the primary amine and an olefin, or via hydrogenolysis to the primary amine and a paraffin (Figure 5). Both pathways are initiated by the dissociative chemisorption of the secondary amine to an alkyl and amine fragment.\(^{101}\) It can be challenging to assess the selectivity for the elimination and hydrogenolysis pathways, as the hydrogenation of olefins to paraffins occurs rapidly on noble metal catalysts.\(^{101}\)

It should be noted, that the ammonia which is formed in the HDN reactions can poison the active sites of the catalyst and suppress the activity for other hydrotreating reactions.\(^{12,36,73}\)
This chapter presents the materials, catalyst preparation methods, catalyst characterization techniques and the catalytic activity testing procedure. Additionally, the analytical methods and calculation procedures are explained.

### 3.1 Materials

The chemicals used for the reactor experiments, calibrations and catalyst preparation are presented in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Purity</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propanol</td>
<td>Riedel de Haën</td>
<td>&gt;99%</td>
<td>I-IV</td>
</tr>
<tr>
<td>Decalin (decahydronaphthalene, anhydrous, mixture of cis and trans)</td>
<td>Sigma Aldrich</td>
<td>&gt;99%</td>
<td>I-III</td>
</tr>
<tr>
<td>Decalin (decahydronaphthalene, cis + trans)</td>
<td>Thermo Scientific</td>
<td>98%</td>
<td>IV</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>Sigma Aldrich, Merck</td>
<td>&gt;99%</td>
<td>I-IV</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>Aldrich</td>
<td>&gt;99%</td>
<td>I</td>
</tr>
<tr>
<td>1-tetradecylamine</td>
<td>Sigma Aldrich</td>
<td>&gt;95%</td>
<td>I</td>
</tr>
<tr>
<td>n-pentadecane</td>
<td>Aldrich</td>
<td>&gt;99%</td>
<td>I-IV</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>Sigma Aldrich</td>
<td>&gt;99%</td>
<td>I-IV</td>
</tr>
<tr>
<td>n-hexadecanamide</td>
<td>Tokyo Chemical Industry</td>
<td>&gt;95%</td>
<td>II-IV</td>
</tr>
<tr>
<td>1-hexadecylamine</td>
<td>Tokyo Chemical Industry</td>
<td>&gt;95%</td>
<td>I-IV</td>
</tr>
<tr>
<td>1-hexadecanol</td>
<td>Acros Organics</td>
<td>96%</td>
<td>I-IV</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>Riedel-de-Haën</td>
<td>&gt;98%</td>
<td>I-IV</td>
</tr>
<tr>
<td>n-pentadecanoniitrile</td>
<td>Tokyo Chemical Industry</td>
<td>&gt;95%</td>
<td>II-IV</td>
</tr>
<tr>
<td>n-heptadecanoniitrile</td>
<td>Tokyo Chemical Industry</td>
<td>&gt;95%</td>
<td>II-IV</td>
</tr>
<tr>
<td>Palmityl palmitate</td>
<td>Sigma-Aldrich</td>
<td>&gt;99%</td>
<td>I-IV</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Sigma-Aldrich</td>
<td>&gt;99%</td>
<td>II-IV</td>
</tr>
<tr>
<td>Pd(II) nitrate solution</td>
<td>Alfa Aesar</td>
<td>12.16 wt. % Pd</td>
<td>III</td>
</tr>
<tr>
<td>Pt(IV) nitrate solution</td>
<td>Alfa Aesar</td>
<td>15 wt. % Pt</td>
<td>I-IV</td>
</tr>
<tr>
<td>Rh(III) nitrate solution</td>
<td>Aldrich</td>
<td>~10 wt. % Rh</td>
<td>III</td>
</tr>
<tr>
<td>Ru(III) nitrosyl nitrate</td>
<td>Alfa Aesar</td>
<td>31.78 wt. % Ru</td>
<td>II, IV</td>
</tr>
<tr>
<td>Ni(II) nitrate hexahydrate</td>
<td>Aldrich</td>
<td>99.99%</td>
<td>II, IV</td>
</tr>
<tr>
<td>Cu(II) nitrate trihydrate</td>
<td>Aldrich</td>
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<td>IV</td>
</tr>
<tr>
<td>Co(II) nitrate hexahydrate</td>
<td>Merck</td>
<td>&gt;99%</td>
<td>IV</td>
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<tr>
<td>TiO$_2$, anatase</td>
<td>Alfa Aesar</td>
<td>n.a.</td>
<td>II</td>
</tr>
<tr>
<td>ZrO$_2$, monoclinic</td>
<td>Saint-Gobain Norpro</td>
<td>n.a.</td>
<td>I-III</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$ (calcin from Boehmite)</td>
<td>Sasol (Pural NW)</td>
<td>n.a.</td>
<td>II</td>
</tr>
<tr>
<td>5SiO$_2$-95Al$_2$O$_3$ (5 wt% SiO$_2$/Al$_2$O$_3$)</td>
<td>Sasol (Siralox5)</td>
<td>n.a.</td>
<td>II</td>
</tr>
<tr>
<td>30SiO$_2$-70Al$_2$O$_3$ (30 wt% SiO$_2$/Al$_2$O$_3$)</td>
<td>Sasol (Siralox30)</td>
<td>n.a.</td>
<td>II</td>
</tr>
</tbody>
</table>
The gases used in this work were acquired from Oy AGA Ab until 10/2021 [II, III], and from Woikoski from 11/2021 onwards [I, II, IV]. They are listed with their purities in Table 3.

### Table 3. Gases used in this work

<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity</th>
<th>Use</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>99.999%</td>
<td>Reactor</td>
<td>I, II, IV</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>99.995%</td>
<td>Reactor</td>
<td>II, III</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>99.999%</td>
<td>Pulse titration</td>
<td>III</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>99.999%</td>
<td>Reactor</td>
<td>I, II, IV</td>
</tr>
<tr>
<td>10 vol. % CO/He</td>
<td>99.999%/99.999%</td>
<td>Pulse titration</td>
<td>I, III, IV</td>
</tr>
<tr>
<td>10 vol. % CO₂/He</td>
<td>99.999%/99.999%</td>
<td>CO₂-TPD (2021)</td>
<td>III</td>
</tr>
<tr>
<td>5.2 vol. % CO₂/He</td>
<td>99.999%/99.999%</td>
<td>CO₂-TPD (2022)</td>
<td>II, IV</td>
</tr>
<tr>
<td>Argon</td>
<td>99.999%</td>
<td>TPR</td>
<td>II-IV</td>
</tr>
<tr>
<td>2% vol. % H₂/Ar</td>
<td>99.999%/99.999%</td>
<td>TPR</td>
<td>II-IV</td>
</tr>
</tbody>
</table>

3.2 Catalyst preparation

The supports used in Publication II were selected based on their diverse acid-base and redox properties, while a relatively low 1 wt. % nominal metal Pt loading was adopted to facilitate the assessment of the impact of the support. The same 1 wt. % nominal loading was later applied for Publication III, to enable a direct comparison with the catalysts of Publication II. The active metals were chosen based on their previously reported activity in both HDO and HDN.\(^\text{38, 96, 100}\) For Publication IV, the noble metal loading was decreased to 0.5 wt. %, as one of the aims was to investigate whether the activity of bimetallic catalysts with a lower noble metal loading can exceed the activity of the monometallic noble metal catalysts. The ratio between noble metal and base metal was adopted from the work by Do et al.\(^\text{53}\)

The used supports were first sieved to a particle size of 0.25-0.42 mm and calcined in ambient air in a static muffle furnace for 10 hours, using the temperatures indicated in Table 4.

The catalysts of Publications I-III were prepared with a vacuum impregnation (VacI) method, as follows. Approximately 2.5 g of calcined support was placed to a 100 ml round-bottom flask and dried at 60 °C under vacuum in a rotary evaporator for 90 min. The aqueous metal precursor solution was prepared with Type 1 ultrapure water, targeting an active metal loading of 1 wt. %. The total volume of the impregnation solution corresponded to approximately 4 times the total pore volume of the support. The precursor solution was introduced dropwise to the support under vacuum at room temperature, while stirring at
120 rpm. The stirring was continued for 2 h, which allowed the excess liquid to evaporate. The catalyst was dried under vacuum the next day, first at 40 °C for 60 min and then at 60 °C for 30 min.

The catalysts of Publication IV were prepared with incipient wetness impregnation (IWI), targeting metal loadings of 0.5 wt. % (Pt and Ru) and 1.5 wt. % (Cu, Co and Ni). The metals were co-impregnated in the preparation of the bimetallic catalysts. The metal precursor solutions were prepared with Type 1 ultrapure water to match the total pore volume of the support. The impregnation solution was introduced dropwise to the support, stirring vigorously between the additions. The catalysts were aged in room temperature overnight, and dried in an oven for 5 hours at 120 °C.

The dried catalysts were calcined in a flow through calcination oven under 100 ml/min synthetic air flow. The calcination was carried out at 450 °C for 1 or 2 h, using a 1-2 °C/min heating ramp, as indicated in Table 4.

### Table 4. Catalyst preparation details

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>Nominal loading (wt.%)</th>
<th>Support calcination</th>
<th>Catalyst calcination</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/ZrO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>I,II</td>
</tr>
<tr>
<td>Pt/ZrO₂ (2nd batch)</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II,III</td>
</tr>
<tr>
<td>Pt/25Ce₂O₇-75ZrO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>450 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II</td>
</tr>
<tr>
<td>Pt/SiO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II</td>
</tr>
<tr>
<td>Pt/γ-Al₂O₃</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II</td>
</tr>
<tr>
<td>Pt/5SiO₂-95Al₂O₃</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>250 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II</td>
</tr>
<tr>
<td>Pt/30SiO₂-70Al₂O₃</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II</td>
</tr>
<tr>
<td>Pt/Nb₂O₅</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>500 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II</td>
</tr>
<tr>
<td>Pt/TiO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>450 °C, 10h</td>
<td>450 °C, 1h, 2°C/min</td>
<td>II</td>
</tr>
<tr>
<td>Ni/ZrO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>III</td>
</tr>
<tr>
<td>Ru/ZrO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>III</td>
</tr>
<tr>
<td>Rh/ZrO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>III</td>
</tr>
<tr>
<td>Pd/ZrO₂</td>
<td>VacI</td>
<td>1.0 wt.%</td>
<td>600 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>III</td>
</tr>
<tr>
<td>Pt/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>0.5 wt.%</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
<tr>
<td>Ru/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>0.5 wt.%</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
<tr>
<td>Ni/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>1.5 wt.%</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
<tr>
<td>Co/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>1.5 wt.%</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
<tr>
<td>Cu/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>1.5 wt.%</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
<tr>
<td>PtNi/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>0.5 wt.% Pt 1.5 wt.% Ni</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
<tr>
<td>RuNi/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>0.5 wt.% Ru 1.5 wt.% Ni</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
<tr>
<td>PtCo/17Ce₂O₇-83ZrO₂</td>
<td>IWI</td>
<td>0.5 wt.% Pt 1.5 wt.% Co</td>
<td>450 °C, 10h</td>
<td>450 °C, 2h, 1°C/min</td>
<td>IV</td>
</tr>
</tbody>
</table>
3.3 Catalyst characterization

3.3.1 N₂-physisorption

A Surfer equipment by Thermo Scientific was used to carry out isothermal N₂-physisorption measurements at -196 °C for 100-200 mg samples of all calcined catalysts [I-IV]. Liquid nitrogen was used as a coolant. In order to remove moisture and other adsorbed compounds, the samples were degassed in vacuum at 350 °C for 180 min before the measurements, using a 5 °C/min heating rate. A dead volume calibration was carried out with He after every measurement. The specific surface area \( S_{BET} \) (m²/g) was calculated from the adsorption isotherm with the Brunauer–Emmett–Teller (BET) method. The specific pore volume \( V_{pore} \) (cm³/g), pore size distribution and mean pore diameter \( d_{p,\text{mean}} \) (nm) were calculated from the desorption branch with the Barrett–Joyner–Halenda (BJH) method.

3.3.2 X-ray fluorescence

A semi-quantitative estimation of the active metal loading (wt. %) was obtained with X-ray fluorescence (XRF), using a wavelength dispersive PANalytical Axios mAx equipment [I-IV]. The measurements were conducted in He for approximately 200 mg samples of ground, calcined catalysts. The samples were measured as loose powders, in Chemplex 1330-SE sample cups covered with a 3.6 µm mylar film.

3.3.3 X-ray diffraction

X-ray diffraction (XRD) measurements were carried out to study the crystallographic phases of the catalysts [II-IV]. The measurements were conducted in a PANalytical X’Pert PRO MPD Alpha-1 X-ray diffractometer, with Cu Kα1 radiation (45 kV, 40 mA). The \( 2\theta \) scanning range was from 5° to 100°, and a step size of 0.026° was used. The analysis was done for ground samples of the calcined catalysts. The HighScore software was used for phase identification (ICDD PDF-4+ 2023 database).

3.3.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed for the catalysts with a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer using a monochromated Al Kα X-ray source (1486.7 eV) run at 100 W [II-IV]. The catalyst samples were reduced ex-situ at 350 °C in 2 vol. % H₂/Ar for 60 min before the measurements and transferred to the equipment through air. The survey spectra were recorded using a pass energy of 80 eV and a step size of 1.0 eV, while the high-resolution spectra were recorded using a pass energy of 20
eV and a step size of 0.1 eV. Photoelectrons were collected at a 90° take-off angle under ultra-high vacuum conditions, with a base pressure below \(1 \cdot 10^{-9}\) Torr. The diameter of the beam spot from the X-ray was 1 mm, and the area of analysis for the measurements was 300 \(\mu\)m \(\times\) 700 \(\mu\)m. All spectra were charge-corrected relative to the position of C–C bonding of carbon at 284.8 eV. Data analysis was performed with the CasaXPS software, as described in Publications II-IV.

3.3.5 Temperature programmed reduction

Qualitative hydrogen temperature-programmed reduction (H\(_2\)-TPR) measurements were carried out for the bare supports and the calcined catalysts with an AMI-200R (Altamira Instruments) flow through equipment, which was connected to a Pfeiffer OmniStar GSD320 mass spectrometer (MS) [II-IV]. The catalyst samples, 70-120 mg, were dried by heating from room temperature to 200 °C in He flow with a heating rate of 10 °C/min, and holding for 120 min. Afterwards, the samples were cooled down to 30°C in He flow. At 30 °C, the samples were flushed in Ar for 30 min. Next, a flow of 2 vol. % H\(_2\)/Ar was directed through the samples, and the temperature was raised to 600 °C with a heating rate of 5°C/min. The total flowrate was kept constant at 50 ml/min (STP) throughout the measurement. Mass-to-charge ratios (m/z) 2 (H\(_2\)), 4 (He), 18 (H\(_2\)O), 28 (N\(_2\)/CO), 32 (O\(_2\)) and 40 (Ar) were monitored with the MS. The data between 30 and 60 °C was disregarded in the data treatment and visualization, due to signal fluctuations attributed to stabilization of the flowrates.

3.3.6 Acid site and basic site characterization

Acid site characterization was carried out for the calcined catalysts with Fourier transform infrared spectroscopy (FTIR), using pyridine as the probe molecule [II-IV]. The measurements were carried out in a Thermo Scientific Nicolet iS10 spectrometer, equipped with an in-situ transmission FTIR cell by Harrick Scientific Products Inc (customized from the HTC-3 model), a liquid-N\(_2\) cooled Mercury-Cadmium-Telluride (MCT) detector and a HeNe laser. The spectral range was 4000-650 cm\(^{-1}\) (0.24 cm\(^{-1}\) spectral resolution).

The catalyst samples (15-30 mg) were pressed into self-supported pellets with a diameter of 1.1 cm, using a hydraulic press. The samples were mounted to the cell, and heated in vacuum to 90 °C with a 5 °C/min heating ramp, where the temperature was maintained for 30 min. Next, the temperature was elevated to 450 °C with a 20 °C/min ramp and kept there for 60 min. The temperature was lowered to 170 °C and held at 170 °C for 10 min, after of which the spectra of the clean samples were collected. The samples were then saturated with pyridine for 10 min, using an atmospheric saturator. This was followed by evacuation and a 15 min flush. The spectra that were used to quantify the acidity were then recorded.

The Omnic 9.11 software was used to subtract the background and the spectra of the clean samples from the spectra of the pyridine-saturated samples, and to carry out a stepwise linear baseline correction. Peak integration and
deconvolution were carried out with Omnic 9.11 and OriginPro, and the concentration of Lewis and Bronsted acid sites were estimated from the corresponding peak areas and sample weight, as described by Emeis.\textsuperscript{108}

Carbon dioxide temperature-programmed desorption (CO\textsubscript{2}-TPD) measurements were conducted for the catalysts to quantify their overall basicity. The measurements were done with the AMI-200R equipment for 70-120 mg catalyst samples. The samples were dried in He for 2 hours at 180 °C, using a heating ramp of 10 °C/min, after of which the samples were heated to 350 °C in 2 vol. % H\textsubscript{2}/Ar, and reduced for 2 hours [II, IV]. After reduction, the samples were cooled down in He to 50 °C and further held for 30 min. Next, a 0.52 vol. % [II, IV] or 1 vol % [III] CO\textsubscript{2}/He flow was directed to the samples at 50 °C, and maintained for 30 min [II, III] or 60 min [IV], after of which the samples were flushed in He for 60 min. Then, the samples were heated to 600 °C [II, III] or 800 °C [IV] in He with a heating rate of 10 °C/min, and kept at the maximum temperature for 30 min, before cooling down. A 50 ml/min (STP) flow was maintained throughout the entire experiment. The desorbed CO\textsubscript{2} was quantified by carrying out a one-step calibration for m/z 44. Additionally, m/z 4 (He), 18 (H\textsubscript{2}O), 28 (N\textsubscript{2}/CO) and 32 (O\textsubscript{2}) were followed with the MS.

3.3.7 Scanning transmission electron microscopy

Scanning transmission electron microscopy (STEM) images were recorded of the calcined catalysts, using a JEOL JEM-2200FS aberration corrected high resolution electron microscope [I-IV]. The equipment was operated at 200 kV acceleration voltage. The samples were drop-casted with acetone on copper grids and coated with ultrathin carbon film before the measurements. Elemental mapping analysis was carried out with an X-ray energy-dispersive spectrometer (EDS) which was coupled to the microscope [III, IV]. The diameter of 100-200 metal particles were measured in Publications I-III using the ImageJ software, in order to estimate the metal particle size distribution and the mean metal particle size $d_m$ (nm).

3.3.8 CO and H\textsubscript{2} pulse chemisorption

Pulse chemisorption measurements were carried out for 100 mg catalyst samples. CO was used as a probe molecule for the Ru/ZrO\textsubscript{2}, Pt/ZrO\textsubscript{2} and Pd/ZrO\textsubscript{2} catalysts [I, III] and for the catalysts supported on 17CeO\textsubscript{2}-83ZrO\textsubscript{2} [IV], whereas H\textsubscript{2} was used for the Ni/ZrO\textsubscript{2} and Rh/ZrO\textsubscript{2} [III]. The pulse chemisorption measurements were performed in the AMI-200R equipment connected to the Pfeiffer OmniStar GSD320 MS.

The samples were first dried at 200 °C in He for 120 min, reduced at 350 °C in 2 vol. % H\textsubscript{2}/Ar for 60 min, cooled down to 50 °C and flushed for 60 min in He. Next, in case of CO pulse chemisorption, 25 pulses (0.505 ml) of 2 or 5 vol. % CO/He, were injected to the samples with 5 min intervals, while monitoring the composition of the outlet gas with the MS (m/z 28 for CO, 44 for CO\textsubscript{2} and 18 for H\textsubscript{2}O). In the case of H\textsubscript{2} pulse chemisorption, 15 pulses (0.505 ml) of 4 vol. % H\textsubscript{2} were injected to the samples with 10 min intervals, while monitoring m/z 2 for
H₂. The pulse loop temperature was 100 °C during the CO pulse chemisorption measurements of Publications I and III, and 30 °C during the H₂ pulse chemisorption measurements and the CO titration measurements of Publication IV. A constant carrier gas flow of 50 ml/min (STP) was maintained throughout the measurements. In Publications I and III, the relations presented in the Handbook of Heterogeneous Catalysis were used to estimate the dispersion $D$ (%) and mean particle size $d_m$ (nm) from the adsorbed amount of probe gas. The calculations were done assuming one chemisorbed CO molecule per surface atom, and one dissociatively chemisorbed H₂ molecule per two surface atoms.

3.4 Catalytic activity tests

The catalytic activity tests were carried out in a 100 ml Hastelloy batch reactor (Parr Instrument Company), equipped with a heated feeding vessel [I-IV].

The catalyst was first dried in-situ at 180 °C under 10 bar of N₂ for 60 min, and reduced at 350 °C under 20 bar of H₂ for 60 min, as illustrated in Figure 6a. The catalyst weight varied from 14 to 80 mg in Publication I, depending on the feed composition, and was typically 20 mg in Publications II-IV.

The feed mixture was prepared by dissolving the desired amount of model compound (n-hexadecanamide, 1-hexadecylamine, 1-tetradecylamine or palmitic acid) to 31 ml of decalin. The mixture was heated to approximately 100 °C under stirring to dissolve the reactants, and a 1 ml zero-sample was taken for analysis.

The feed mixture was released to the pre-heated reactor via the feed vessel. The reactor was pressurized with H₂ and stirring was initiated, marking the onset of the reaction time. For most experiments, a reaction temperature of 300 °C, pressure of 80 bar H₂, and stirring speed of 600 rpm was used. The stirring was stopped and the reactor was quenched with an ice bath once the reaction time had elapsed (15-300 min). Figure 6b illustrates the activity test procedure. A reaction time of 60 min was used for the assessment of the influence of the feed composition [I] and for the activity comparison of the
different catalysts [II-IV]. This corresponded to a batch residence time of 0.37-0.39 g<sub>cat</sub>/g<sub>reactants</sub>. The batch residence time, \( \tau (g_{cat}/g_{reactants}) \), is defined as the mass of catalyst (\( m_{cat}, g \)) multiplied by reaction time (\( t, h \)) and divided by mass of reactant(s) (\( m_{A,0}, g \)), as indicated in Equation (1).

\[
\tau = \frac{m_{cat}}{m_{A,0}}
\]  

(1)

### 3.5 Product analysis

Prior analysis, the reactant and product samples (1 mL) were finalized by the addition of a second solvent, 2-propanol (0.18 mL) and an internal standard, n-dodecane (6 µl) [I-IV]. The second solvent was added to prevent precipitation of the reactant and reaction products.

#### 3.5.1 Product identification

The reaction products were identified with gas chromatography-mass spectrometry (GC-MS) [I-III]. The GC-MS measurements were performed with a Shimadzu QP2010SE gas chromatograph mass spectrometer with EI ionization and an Optic 4 injector. The tool was equipped with an Agilent J&W HP5-MS column (30 m × 0.25 mm × 0.25 µm). The NIST2017 library was used to identify the products.

#### 3.5.2 Product quantification

The liquid reaction products of were quantified using an Agilent 7890 gas chromatograph (GC), equipped with an Agilent J&W HP5-MS column (30 m × 0.25 mm × 0.25 µm) [II, III] or an Agilent J&W HP1-MS column (60 m × 0.25 mm × 0.25 µm) [I, II, IV], with the outlet split to a flame ionization detector (FID) and a nitrogen phosphorus detector (NPD). Detailed descriptions of the analysis programs are available in Publications I-III.

The reactant conversion \( X_A (%) \) was calculated with Equation (2),

\[
X_A = \frac{n_{A,0} - n_A}{n_{A,0}} \cdot 100\%,
\]

(2)

where \( n_{A,0} \) is the initial amount of reactant (mol) and \( n_A \) is the amount of unreacted reactant in the product sample (mol).

The product distribution of the C14 amine and C16 acid co-hydrotreating experiments [I] was calculated using Equation (3),

\[
c_i = \frac{n_i}{n_{amine+acid,0}} \cdot 100\%,
\]

(3)

where \( c_i \) is the molar share of compound \( i \) in the reaction products (mol %), \( n_i \) is the amount of compound \( i \) in the reaction products (mol), and \( n_{amine+acid,0} \) is the total amount of C14 amine and C16 acid in the reaction mixture (mol). The
unreacted reactants were included in the product distribution of the C14 amine and C16 acid co-hydrotreating experiments [I].

The yield for each product $Y_i$ (%) of the $n$-hexadecanamide hydrotreating experiments [II-IV] was calculated with Equation (4),

$$Y_i = \frac{\mu_in_i}{n_{A,0}} \cdot 100\%,$$  (4)

where $\mu_i$ is a stoichiometric factor (2 for the C32 compounds and 1 for the other products) and $n_i$ is the amount of product $i$ in the product sample (mol).

The oxygen removal ($O$-removal, %) of the $n$-hexadecanamide hydrotreating experiments [II-IV] was estimated from the product distribution using Equation (5),

$$O\text{-removal} = \frac{c_{O,\text{products}}}{c_{O,\text{feed}}} \cdot 100\%,$$  (5)

where $c_{O,\text{products}}$ and $c_{O,\text{feed}}$ are the oxygen contents estimated from the composition of the product sample and the feed mixture, respectively (ppm). The unit ppm is defined as mg/L in this work.

The molar carbon balance closure $B_C$ was calculated using Equation (6),

$$B_C = \frac{n_{C,\text{products}}}{n_{C,\text{feed}}} \cdot 100\%,$$  (6)

where $n_{C,\text{products}}$ is the amount of carbon quantified from the product mixture (mol) and $n_{C,\text{feed}}$ is the amount of carbon quantified from the feed mixture (mol). The carbon balance closure typically exceeded 90% [I-IV].

### 3.5.3 Total nitrogen content analysis

An AntekPAC ElemeNtS analyzer was used to measure the total nitrogen content of the samples [I-IV]. The equipment was calibrated for nitrogen contents between 0 and 1000 ppm with calibration solutions obtained from AC Analytical Controls BV. The nitrogen removal ($N$-removal, %) was calculated using Equation (7),

$$N\text{-removal} = \frac{c_{N,\text{products}}}{c_{N,\text{feed}}} \cdot 100\%,$$  (7)

where $c_{N,\text{products}}$ is the nitrogen content of the product sample (ppm) and $c_{N,\text{feed}}$ is the nitrogen content of the feed mixture (ppm).
4. Catalyst characterization

This chapter presents characterization data of the prepared catalysts. Section 4.1 displays the characterization data of the Pt catalysts on different oxide supports [II] and of the metal catalysts supported on ZrO$_2$ [III]. The properties of the monometallic and bimetallic catalysts supported on 17CeO$_2$-83ZrO$_2$ [IV] are discussed in Section 4.2.

4.1 Pt supported on different oxides and different metals supported on ZrO$_2$

Table 5 presents characterization results for the Pt catalysts on different oxide supports [II] and the metal catalysts supported on ZrO$_2$ [III]. The table includes the specific surface area, specific pore volume and mean pore diameter from N$_2$-physisorption measurements, the desorbed amount of CO$_2$ from CO$_2$-TPD measurements, the amounts of pyridine adsorbed on Lewis acid sites (LAS) and Bronsted acid sites (BAS) from the acid site characterization via FTIR spectroscopy of pyridine adsorbed pyridine, and the mean metal particle size derived from STEM images or pulse chemisorption measurements. The value shown in the parenthesis after the mean metal particle size based on the STEM analysis, is the standard deviation.
The porous properties of the catalysts varied significantly, depending on the used support (Table 5). For example, the catalysts supported on ZrO₂ had the lowest specific surface area (42-50 m²/g) and largest mean pore diameter (19-20 nm). The Pt catalysts supported on SiO₂, 5SiO₂-95Al₂O₃ and 30SiO₂-70Al₂O₃ had the largest specific surface area (266-315 m²/g) and highest specific pore volume (0.60-0.98 cm³/g). The Pt/Nb₂O₅, Pt/5SiO₂-95Al₂O₃ and Pt/30SiO₂-70Al₂O₃ catalysts had the lowest mean pore diameter (6-8 nm) out of the studied catalysts.

X-ray diffraction was used to identify the crystallographic phase of the catalysts. The X-ray diffractograms of the calcined catalysts did not contain reflections characteristic to the active metals, which may indicate that the metals were well dispersed before the reduction [II, III].

The desired γ-phase for the Al₂O₃ support was confirmed for Pt/γ-Al₂O₃ (ICDD 01-075-0921) [II]. The reflections in the X-ray diffractograms of the Pt/ZrO₂, Pd/ZrO₂, Rh/ZrO₂, Ru/ZrO₂ and Ni/ZrO₂ catalysts corresponded to monoclinic ZrO₂ (ICDD 00-007-0343) [I-III]. A monoclinic phase for the support was likewise observed for Pt/Nb₂O₅ (ICDD 00-027-1312), while the reflections of
Pt/TiO$_2$ corresponded to anatase TiO$_2$ (ICDD 01-083-5914) [II]. The reflections of the X-ray diffractogram for the Pt/25CeO$_2$−75ZrO$_2$ catalyst matched Ce$_{0.20}$Zr$_{0.80}$O$_2$ with a tetragonal phase (ICDD 04-002-5421) [II].

The semi-quantitative XRF measurements of the catalysts indicated metal loadings of 0.6 wt. % for Pt/5SiO$_2$−95Al$_2$O$_3$, Pt/30SiO$_2$−70Al$_2$O$_3$, Pt/ZrO$_2$ and Pd/ZrO$_2$ [II, III]. The analysis gave a metal loading of 0.7 wt. % for Pt/SiO$_2$, Pt/γ-Al$_2$O$_3$, Ni/ZrO$_2$, Ru/ZrO$_2$ and Rh/ZrO$_2$, while a metal loading of 0.8 wt. % was obtained for Pt/25CeO$_2$−75ZrO$_2$, Pt/Nb$_2$O$_5$ and Pt/TiO$_2$ [II, III]. These values are within the measurement uncertainty of each other.

STEM images were recorded of the supported Pt catalysts, in order to derive the mean Pt particle size and the particle size distribution. The mean Pt particle size of the supported Pt catalysts ranged between 1.5 and 2.1 nm (Table 5), and the difference between the mean particle size of the supported Pt catalysts was within the standard deviation of the measurements (0.5–1 nm). The Pt dispersion therefore appeared to be similar on all supported Pt catalysts.

Based on the pulse chemisorption measurements, the mean metal particle size of the Rh/ZrO$_2$, Ru/ZrO$_2$ and Pd/ZrO$_2$ catalysts ranged between 1.9 and 2.9 nm (Table 5). Due to the uncertainty of the semi-quantitative elemental analysis, the calculations were done using the nominal metal loading (1 wt. %), which implies that the values are within the measurement accuracy of each other. Based on the H$_2$ chemisorption measurement, the mean metal particle size of the Ni/ZrO$_2$ catalyst was considerably higher, 30 nm. This may also reflect an incomplete reduction of Ni [III].

H$_2$-TPR measurements were carried out to qualitatively study the reducibility and reducible species of the catalysts. Figure 7 displays the H$_2$-TPR profiles of the bare supports and the calcined supported metal catalysts.
Catalyst characterization

Figure 7. H$_2$-TPR profiles of the bare supports and the calcined supported metal catalysts. The data is from Publications II and III.

The H$_2$-TPR profiles of the bare 25CeO$_2$-75ZrO$_2$ and TiO$_2$ supports contained reduction peaks at 560 and 450 °C, related to the partial reduction of CeO$_2$ and TiO$_2$, respectively (Figure 7) [II].$^{94,111-114}$ The support-related reduction peaks were shifted to lower temperatures on the Pt/25CeO$_2$-75ZrO$_2$ and Pt/TiO$_2$ catalysts, which indicates that Pt enhanced the reducibility of the support, potentially due to H$_2$ spillover.$^{94,111,112}$

The reduction of PtO$_2$ to metallic Pt occurred below 200 °C on all calcined supported Pt catalysts (Figure 7). Considering the absence of major reduction peaks on the Pt/SiO$_2$, Pt/γ-Al$_2$O$_3$, Pt/5SiO$_2$-95Al$_2$O$_3$, Pt/30SiO$_2$-70Al$_2$O$_3$, and Pt/Nb$_2$O$_5$ catalysts, it is possible that the Pt got reduced immediately upon the introduction of H$_2$ at the start of the temperature ramp, or that the Pt already was metallic after the calcination [II]. XPS analysis of Pt catalyst samples that had been reduced ex-situ in H$_2$ at 350 °C, indicated that the oxidation state of Pt was similar on all supported Pt catalysts [II]. The majority of the Pt present as Pt(0) on the studied catalysts, with no more than 6% of the Pt present as Pt(II) and Pt(IV), each [II].

From the H$_2$-TPR profiles in Figure 7, it can be seen that the reduction of the Ru, Rh and Pd oxides on the Ru/ZrO$_2$, Rh/ZrO$_2$ and Pd/ZrO$_2$ catalysts,
respectively, occurred more than 100 °C below 350 °C, i.e., the reduction temperature that was used in the reactor experiments [III]. The Ru, Rh and Pd were therefore assumed to be metallic in the activity tests.

The H₂-TPR profile of the Ni/ZrO₂ catalyst contained broad reduction peaks, which reached their maximum intensity at approximately 240 and 425 °C, respectively (Figure 7). The first reduction peak may have been related to the reduction of NiO particles with weak interactions with the ZrO₂ support. The high-temperature peak may have corresponded to the reduction of NiO particles interacting more strongly with the ZrO₂ support, or the reduction of Ni²⁺ species in the ZrO₂ lattice. It is possible that not all of the Ni on the Ni/ZrO₂ catalyst was reduced at the reaction conditions [III].

Acid site characterization was carried out via FTIR spectroscopy, using pyridine as the probe molecule [II, III]. The FTIR spectra of the pyridine-saturated supported metal catalysts are displayed in Figure 8.

![Figure 8](image)

**Figure 8.** Transmission FTIR spectra for the pyridine-saturated supported metal catalysts, with the background and spectra of the clean samples subtracted. The spectra were collected at 170 °C. The vertical lines indicate the vibration bands characteristic for pyridine adsorbed on Brønsted acid sites (1545, 1540 cm⁻¹) and Lewis acid sites (1453-1442 cm⁻¹). The data of the Figure is from Publications II and III.

The pyridine FTIR measurements indicated that the catalysts were predominantly Lewis acidic, but both the concentration and strength of the Lewis acid sites varied between the catalysts (Figure 8, Table 5) [II, III]. The Brønsted acid site concentration was below 30 µmol/g for all studied catalysts except for Pt/30SiO₂-70Al₂O₃, Pt/Nb₂O₅ and Rh/ZrO₂.

The catalysts were divided into four groups based on the strength of their Lewis acid sites. The Pt/30SiO₂-70Al₂O₃, Pt/5SiO₂-95Al₂O₃ and Pt/γ-Al₂O₃ catalysts comprised the first group, referred to as Si-Al. The vibration bands characteristic for pyridine adsorbed on Lewis acid sites were located at 1453 cm⁻¹.
The catalysts that belonged to the Si-Al group had the strongest Lewis acid sites out of the studied catalysts. The Pt/30SiO$_2$-70Al$_2$O$_3$ catalyst additionally contained 30 µmol/g Brønsted acid sites. In the case of Pt/Nb$_2$O$_5$ and Pt/TiO$_2$, the vibration band related to pyridine adsorbed on Lewis acid sites was shifted to a lower wavenumber (1446 cm$^{-1}$) compared to the catalysts of the Si-Al group (Figure 8). This indicates Lewis acid sites of intermediate strength. Pt/Nb$_2$O$_5$ and Pt/TiO$_2$ therefore formed the Ti-Nb group. The Pt/Nb$_2$O$_5$ catalyst furthermore contained 90 µmol/g of weak Brønsted acid sites.

Pt/ZrO$_2$ and Pt/CeO$_2$-ZrO$_2$, denoted Ce-Zr, contained the weakest Lewis acid sites out of the supported Pt catalysts, and the main vibration band of pyridine adsorbed on Lewis acid sites was located at 1442 cm$^{-1}$ for both catalysts. The strength of the Lewis acid sites of the ZrO$_2$-supported Ru, Rh, Pd and Ni catalysts was similar to Pt/ZrO$_2$. Thus, these catalysts were assigned to the Ce-Zr group. The FTIR spectra of Pt/CoO$_2$-ZrO$_2$ contained another vibration band at 1420 cm$^{-1}$, possibly attributed to hydrogen-bonded pyridine or to pyridine adsorbed on weaker Lewis acid sites, e.g., Ce$^{3+}$ cations. No pyridine adsorption was detected on Pt/SiO$_2$ (Table 5).

CO$_2$-TPD measurements were carried out in order to obtain a measure of the total basicity of the catalysts. The CO$_2$-TPD profiles of the supported metal catalysts are presented in Figure 9, while the total basic site concentration, derived from the amount of desorbed CO$_2$, is presented in Table 5.

![CO$_2$-TPD profiles](image)

**Figure 9.** CO$_2$-TPD profiles of the supported metal catalysts. The data is from Publications II and III.

As can be seen from Table 5, the total basic site concentration was below 100 µmol/g$_{\text{cat}}$ for the studied catalysts, with the exception of Pt/25CeO$_2$-75ZrO$_2$ (210 µmol/g$_{\text{cat}}$) [II, III]. The groups Si-Al and Ti-Nb therefore had a lower total
basic site concentration than total acid site concentration, while the total basic site concentration was comparable with the total acid site concentration for the Ce-Zr group. The catalysts of the Ce-Zr group also contained the strongest basic sites out of the samples, as indicated by a higher CO$_2$ desorption temperature compared to the catalysts of the other groups (Figure 9). No CO$_2$ desorption was detected on Pt/SiO$_2$, which indicates that the basic site concentration was negligible.

To summarize, the Pt catalysts supported on different oxides exhibited differences in the porous properties (Table 5), reducibility (Figure 7), in the concentration and strength of Lewis acid sites and Brønsted acid sites (Table 5, Figure 8), and in the concentration and strength of basic sites (Table 5, Figure 9). Meanwhile, the Pt particle size (Table 5) and the oxidation state of Pt were similar between the catalysts [II].

The ZrO$_2$-supported metal catalysts had similar porous properties and crystallographic phases, and exhibited relatively small differences in the acid–base properties (Table 5). The mean metal particle size of the ZrO$_2$-supported Pt, Pd, Ru and Rh catalysts was within the measurement accuracy of each other. The Ni/ZrO$_2$ catalyst, on the other hand, exhibited a poor reducibility of Ni and a considerably larger mean particle size compared to the noble metals.

### 4.2 Ceria-zirconia supported monometallic and bimetallic catalysts

Table 6 presents the target metal content, metal content based on the semi-quantitative XRF measurements, and the specific surface area, specific pore volume and mean pore size from N$_2$-physisorption measurements for the bare 17CeO$_2$-83ZrO$_2$ support and the monometallic and bimetallic catalysts supported on 17CeO$_2$-83ZrO$_2$. Table 6 additionally indicates the amount of desorbed CO$_2$ from CO$_2$-TPD measurements, amounts of pyridine adsorbed on Lewis and Brønsted acid sites from pyridine FTIR measurements, and the CO adsorption capacity from CO pulse titration measurements for the samples.
Table 6. Properties of the monometallic and bimetallic catalysts supported on 17CeO$_2$-83ZrO$_2$ based on XRF, N$_2$-physisorption, CO$_2$-TPD, pyridine FTIR and CO pulse titration measurements [IV]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Target loading (wt.%)</th>
<th>XRF (wt.%)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{pore}$ (cm$^3$/g)</th>
<th>$d_{p,mean}$ (nm)</th>
<th>Des. CO$_2$ (µmol/g)</th>
<th>LAS (µmol/g)</th>
<th>BAS (µmol/g)</th>
<th>CO ads. capacity (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17CeO$_2$-83ZrO$_2$</td>
<td>-</td>
<td>-</td>
<td>87</td>
<td>0.19</td>
<td>8.2</td>
<td>130</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>0.5</td>
<td>0.3</td>
<td>85</td>
<td>0.21</td>
<td>7.9</td>
<td>160</td>
<td>40</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>Ru</td>
<td>0.5</td>
<td>1.0</td>
<td>87</td>
<td>0.20</td>
<td>8.1</td>
<td>170</td>
<td>50</td>
<td>-</td>
<td>78</td>
</tr>
<tr>
<td>Ni</td>
<td>1.5</td>
<td>1.2</td>
<td>78</td>
<td>0.19</td>
<td>8.1</td>
<td>200</td>
<td>140</td>
<td>15</td>
<td>8</td>
</tr>
<tr>
<td>Co</td>
<td>1.5</td>
<td>1.2</td>
<td>83</td>
<td>0.18</td>
<td>8.1</td>
<td>220</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5</td>
<td>1.1</td>
<td>83</td>
<td>0.20</td>
<td>8.1</td>
<td>170</td>
<td>250</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RuNi</td>
<td>0.5$<em>{Ru}$, 1.5$</em>{Ni}$</td>
<td>0.8$<em>{Ru}$, 1.1$</em>{Ni}$</td>
<td>81</td>
<td>0.18</td>
<td>8.5</td>
<td>160</td>
<td>160</td>
<td>30</td>
<td>148</td>
</tr>
<tr>
<td>PtNi</td>
<td>0.5$<em>{Pt}$, 1.5$</em>{Ni}$</td>
<td>0.3$<em>{Pt}$, 1.2$</em>{Ni}$</td>
<td>81</td>
<td>0.17</td>
<td>8.3</td>
<td>210</td>
<td>130</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>PtCo</td>
<td>0.5$<em>{Pt}$, 1.5$</em>{Co}$</td>
<td>0.3$<em>{Pt}$, 1.2$</em>{Co}$</td>
<td>88</td>
<td>0.21</td>
<td>7.8</td>
<td>180</td>
<td>90</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>PtCu</td>
<td>0.5$<em>{Pt}$, 1.5$</em>{Cu}$</td>
<td>0.3$<em>{Pt}$, 1.2$</em>{Cu}$</td>
<td>83</td>
<td>0.20</td>
<td>7.9</td>
<td>160</td>
<td>220</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>

The semi-quantitative XRF measurements indicated that the metal contents of the bimetallic catalysts were comparable to the sum of the metal content of the corresponding monometallic catalysts (Table 6). The crystallographic and porous properties of the catalysts were similar, based on the XRD [IV] and N$_2$-physisorption measurements (Table 6). The X-ray diffraction patterns of the calcined catalysts contained only reflections corresponding to tetragonal Ce$_{0.13}$Zr$_{0.17}$O$_2$ (ICDD 04-026-5667) [IV]. The lack of metal-related reflections may suggest that the metals were well dispersed before the reduction.

The reducibility of the catalysts was qualitatively studied via H$_2$-TPR measurements. The reduction profiles are presented in Figure 10.
The H$_2$-TPR profiles of the bimetallic catalysts did not equal the superposition of the monometallic catalysts, which is indicative of interactions between the active metals (Figure 10). The Pt and Ru enhanced the reducibility of the Cu, Co and Ni, possibly due to H$_2$ spillover. The active metals likewise decreased the reduction temperature of the 17CeO$_2$-83ZrO$_2$ support. As the reduction of the metal(s) and the support may have occurred simultaneously, the peaks of the H$_2$-TPR profiles could not be reliably assigned to the reduction of specific metal species.

The impregnation of the active metals increased the concentration of both Lewis acid sites and basic sites on most catalysts, compared to the bare 17CeO$_2$-83ZrO$_2$ support (Table 6). Brønsted acid sites (15-30 µmol/g) were only detected on the RuNi, PtNi and Ni catalysts. The Lewis acid site strength was not significantly affected between the catalysts and the bare 17CeO$_2$-83ZrO$_2$ support. In contrast, the basic sites and/or the Lewis-acid basic site pairs were somewhat stronger on the catalysts than on the bare support, based on an elevated CO$_2$ desorption temperature in the CO$_2$-TPD profiles [IV]. The CO$_2$-TPD profiles of the monometallic and bimetallic catalysts and the bare 17CeO$_2$-83ZrO$_2$ are presented in Figure 11. The deconvoluted components are also shown for each sample.
The CO adsorption capacity of the bimetallic RuNi and PtNi catalysts considerably exceeded the sum of the CO adsorption capacity of the monometallic Ni, Ru and Pt catalysts, which may hint towards an increased number of metal sites and an increased metal dispersion (Table 6).\textsuperscript{52,53} The CO adsorption capacity of the PtCo catalyst likewise exceeded the CO adsorption capacity of the monometallic Pt and Co catalysts, but the difference was smaller than in the case of PtNi and RuNi. However, as the CO adsorption stoichiometry likely differed between the catalysts, the CO adsorption capacity should not be regarded as a direct measure of the number of metal sites. For example, reduced Cu does not chemisorb CO, while the CO adsorption stoichiometry on Co depends on the catalyst composition.\textsuperscript{123,124}

XPS measurements were carried out to study the chemical state of the catalyst surface. The samples were reduced ex-situ in H\textsubscript{2} at 350 °C for 60 min and transferred to the equipment in atmosphere. Table 7 presents the active metal surface concentration, surface and nominal bulk ratios of noble metal to base metal, and the ratio of active metals to Ce and Zr for the catalysts.
Table 7. The XPS-derived surface concentration of active metal, ratio of the active metals on the surface, the nominal atomic bulk ratio of active metals, and the ratio of active metals to Ce and Zr [IV]. \( M_1 = \text{Pt or Ru}, \ M_2 = \text{Ni, Co or Cu} \)

<table>
<thead>
<tr>
<th>Catalyst*</th>
<th>Surface concentration of ( M_1 ) and ( M_2 ) (at. %)</th>
<th>( M_1/M_2 ) ratio, XPS</th>
<th>( M_1/M_2 ) ratio, nominal</th>
<th>( (M_1+M_2)/(\text{Ce+Zr}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17CeO(_2)-83ZrO(_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>5.0 at. %</td>
<td>-</td>
<td>-</td>
<td>0.17</td>
</tr>
<tr>
<td>Ru</td>
<td>1.2 at. %</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>Ni</td>
<td>0.6 at. %</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Co</td>
<td>0.9 at. %</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5 at. %</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>RuNi</td>
<td>1.1 at. % Ru \ 0.9 at. % Ni</td>
<td>1.15</td>
<td>0.19</td>
<td>0.07</td>
</tr>
<tr>
<td>PtNi</td>
<td>2.5 at. % Pt \ 4.2 at. % Ni</td>
<td>0.59</td>
<td>0.10</td>
<td>0.24</td>
</tr>
<tr>
<td>PtCo</td>
<td>3.0 at. % Pt \ 3.3 at. % Co</td>
<td>0.91</td>
<td>0.10</td>
<td>0.24</td>
</tr>
<tr>
<td>PtCu</td>
<td>2.0 at. % Pt \ 3.4 at. % Cu</td>
<td>0.59</td>
<td>0.11</td>
<td>0.19</td>
</tr>
</tbody>
</table>

*The samples were reduced ex-situ in H\(_2\) at 350 °C before the measurements and transferred to the equipment through air

*b) Includes adventitious carbon contamination

The co-impregnation of Pt with the base metals (Ni, Co or Cu) decreased the surface concentration of Pt by \(1/3\)-\(1/2\) compared to the monometallic catalysts (Table 6, Table 7). Meanwhile, the surface concentration of the base metals increased by a factor of 4-7, relative to the monometallic samples. In contrast, the surface concentration of Ru and Ni did not markedly change on the RuNi catalyst, compared to the monometallic Ru and Ni catalysts. The atomic surface ratio between the noble metal and the base metal was 5-9 times higher than the nominal bulk elemental ratio. This reflects the enrichment of Pt and Ru on the surface of the catalysts. The atomic ratio of active metal(s) to Ce and Zr was the highest on the surface of the Pt-containing catalysts.

Binding energy shifts were identified in the XPS spectra of the Pt 4f, Cu 2p and Co 2p regions of the monometallic and bimetallic catalysts, which could reflect electronic interactions between the active metals [IV]. For example, the XPS spectra of the Pt 4f region of the Pt, PtNi, PtCo and PtCu catalysts are presented in Figure 12. The deconvoluted platinum components are displayed for each sample, in addition to the measured XPS spectra.
The Pt $4f_{7/2}$ component of Pt(0) was shifted to a 0.4 and 0.2 eV higher binding energy on PtCo and PtNi, respectively, compared to the monometallic Pt catalyst (Figure 12). Meanwhile, the peaks associated with CoO were shifted to a 0.3-0.4 eV lower binding energy in the Co 2p spectra of PtCo compared to the monometallic Co [IV]. The binding energy of the peak related to CuO was 0.4 eV higher in the Cu 2p spectra of PtCu than in the Cu 2p spectra of the monometallic Cu [IV]. No significant binding energy shifts were observed in the Ni 2p and Ru 3d spectra, but the uncertainty should be regarded as significant, due to the oxidation of the active metals that occurred during the sample transfer to the XPS [IV].

To summarize, the monometallic and bimetallic catalysts supported on 17CeO$_2$–83ZrO$_2$ had similar porous properties and comparable metal contents, but exhibited some variability in the concentration of acid and basic sites (Table 6). The variation in the acid–base properties was, nevertheless, lower compared to the Pt catalysts on the different oxide supports (Table 5). The H$_2$-TPR (Figure 11) and XPS (Figure 12) measurements were indicative of interactions between the active metals on the bimetallic catalysts. The CO pulse titration measurements suggested an increased number of surface metal sites on the bimetallic PtCo, PtNi and RuNi catalysts, compared to the respective monometallic catalysts.

Figure 12. High resolution X-ray photoelectron spectra of the Pt 4f region of the Pt, PtCu, PtCo and PtNi catalysts. The samples were reduced ex-situ in H$_2$ at 350 °C before the measurements and transferred to the equipment through air. Modified from Publication IV.
Competitive HDN and HDO reactions were studied by co-hydrotreating palmitic acid (C16 acid) and 1-tetradecylamine (C14 amine) over a 1 wt% Pt/ZrO₂ catalyst [I]. Section 5.1 introduces the products and reactions of the co-hydrotreating experiments. The main purpose of the co-hydrotreating experiments was to study the reactivity of the model compounds, and to gain an understanding on the effect of the feed composition on the activity and selectivity for HDO and HDN in the co-hydrotreating reaction network. These topics are addressed in Section 5.2. The influence of the reaction temperature and the H₂ pressure is discussed in Section 5.3.

5.1 Product distribution

The individual C16 acid HDO experiment gave n-pentadecane (C15 paraffin), n-hexadecane (C16 paraffin), 1-hexadecanol (C16 alcohol), methyl palmitate (C17 ester) and palmityl palmitate (C32 ester), while the individual C14 amine HDN experiment gave n-tetradecane (C14 paraffin) and n-tetradecyl tetradecylamine (C28 amine) [I]. The hydrotreatment of fatty acids and alkyl amines is discussed on a general level in Sections 2.2 and 2.3, respectively.

Co-hydrotreating the C16 acid and the C14 amine expanded the reaction network and changed the favored reaction pathways from the individual HDN and HDO experiments, which was reflected by changes in the conversion and product distribution of both reactants, relative to the individual C14 amine HDN and C16 acid HDO experiments [I]. The products of the co-hydrotreating experiments contained all compounds that were identified in the individual C16 acid HDO and C14 amine HDN experiments, as well as compounds originating from reactions between the C14 amine, the C16 acid and the C16 acid derivatives [I]. These products included 1-tetradecanol (C₁₄ alcohol), 1-hexadecylamine (C₁₆ amine), n-tetradecyl hexadecylamine (C₃₀ amine), n-tetradecyl hexadecanamide (C₳₀ amide) and n-hexadecyl hexadecylamine (C₳₂ amine) [I]. The product sample of the co-hydrotreating experiment on the bare ZrO₂ support additionally contained n-hexadecanal (C₁₆ aldehyde) [I].
Figure 13a displays the product distribution of a C16 acid and C14 amine co-hydrotreating experiment with 80 ppm of both oxygen and nitrogen in the feed as a function of batch residence time. This feed composition corresponds to 30 mol% C16 acid and 70 mol% C14 amine. The batch residence time series data has been broken up to smaller units in Figure 13b-d. Figure 13e shows the conversion as a function of batch residence time, while the paraffin yields and nitrogen removal are presented in Figure 13f.

Figure 13. The (a) overall product distribution, (b) C16 acid-related product distribution, (c) C14 amine-related product distribution, (d) concentration of the condensation products, (e) C14 amine and C16 acid conversions and (f) C14 amine- and C16 acid-originating paraffin yields and nitrogen removal as a function of batch residence time, obtained from hydrotreating a mixture of the C14 amine and C16 acid with 80 ppm of oxygen and 80 ppm of nitrogen on Pt/ZrO2 at 300 °C and 80 bar H2. The lines have been added to guide the eye. Modified from Publication I.

Figure 13b and Figure 13c display the product distribution of the HDO- and HDN-related intermediates, respectively. The steep rise of the C16 alcohol concentration suggested that the HDO of the C16 acid to the C16 alcohol was the initially dominating reaction in the co-hydrotreating system (Figure 13a-b).
The C15 paraffin and the C16 paraffin were initially formed in similar amounts (Figure 13b). After batch residence time 0.2 g\text{cat}/g\text{reactants}, the C16 paraffin concentration increased sharply, while the C15 paraffin concentration stabilized. The stabilization of the C15 paraffin yield coincided with the complete consumption of the C16 acid, implying that the compound only was formed via the decarboxylation of the C16 acid and decarbonylation of the C16 aldehyde. The C16 paraffin, which was formed from the HDO of the C16 alcohol and the decomposition of the C30 condensation products, was the dominant C16 acid-originating final product.

The initial importance of the condensation reactions in the co-hydrotreating experiments is highlighted in Figure 13c. The combined concentration of the nitrogen-containing condensation products (C28 amine, C30 amine, C30 amide), exceeded the concentration of the C14 paraffin until batch residence time point 0.39 g\text{cat}/g\text{reactants}, after which the condensation product concentration first stabilized, and then started decreasing, while the C14 paraffin concentration steadily increased. The changes in the C14 amine concentration were rather small during the last batch residence time points, which possibly could be explained by its consumption towards HDN being balanced out by its re-formation from the condensation products. The product samples did not contain n-tridecane or other shorter chain n-paraffins, which indicates that the Pt/ZrO$_2$ catalyst did not exhibit activity for C‒C bond cleavage routes of the C14 amine, or for the further C‒C bond cleavage of the paraffins.

The evolution of the nitrogen-containing condensation products is visualized in Figure 13d. The C30 amide was readily formed via condensation of the C16 acid and the C14 amine, as long as the C16 acid was present in the product mixture. The maximum concentration of the C30 amide was thus reached by batch residence time point 0.39 g\text{cat}/g\text{reactants}, and by batch residence time point 1.2 g\text{cat}/g\text{reactants}, no C30 amide could be detected from the product sample anymore.

The C28 amine was primarily formed via the disproportionation of the C14 amine, while the C30 amine was formed via the condensation of the C16 alcohol and the C14 amine, from the C16 aldehyde and the C16 amine, and as a product of the HDO of the C30 amide. The shapes of the C28 and C30 amine product distribution curves were similar, despite their different formation pathways (Figure 13d). The net formation of the secondary amines exceeded their net decomposition until batch residence time point 0.75 g\text{cat}/g\text{reactants}, which coincides with the consumption of the oxygen-containing intermediate products. The secondary amines eventually underwent HDN, forming the C14 and C16 paraffins.

The differences in the reactivity of the C14 amine and C16 acid, and the accumulation of the final products are visualized in Figure 13e and Figure 13f, respectively. The C16 acid conversion was higher than the C14 amine conversion throughout the studied batch residence time points (Figure 13e), and the combined C15 and C16 paraffin yield exceeded the C14 paraffin yield.
systematically (Figure 13f). The HDO of the C16 acid thus proceeded more efficiently than the HDN of the C14 amine in the co-hydrotreating system.

5.2 The effect of the feed composition

The effect of the feed composition on the reactivity and selectivity was studied by carrying out a set of co-hydrotreating experiments for the C14 amine and the C16 acid at 300 °C, 80 bar H₂ and a constant batch residence time of 0.39 gcat/h/greactants. The initial nitrogen content was maintained at 80 ppm, while the oxygen content was increased from 40 ppm to 720 ppm. For reference, individual HDN and HDO experiments were carried out at similar batch residence times, with 80 ppm nitrogen and 720 ppm oxygen in the feed, respectively [I]. Figure 14 displays the reactant conversions (a), the paraffin yields originating from the C16 acid and the C14 amine (b), the nitrogen removal relative to the C14 amine conversion (c) and amount of the C30 condensation products (d), as a function of the molar fraction of the C16 acid in the feed (xacid).

![Figure 14](image)

**Figure 14.** The reactant conversions (a), paraffin yields originating from the C16 acid and the C14 amine (b), the nitrogen removal relative to amine conversion (c), and the amount of C30 condensation products (d), as a function of the molar fraction of C16 acid in the reactive feed (C14 amine, C16 acid). The experiments were carried out at 300 °C, 80 bar H₂, and at \( \tau=0.39 \) gcat/h/greactants. Reproduced from Publication I (licensed under CC BY 4.0).

The C16 acid conversion exceeded the C14 amine conversion for all studied feed compositions, and the lowest C16 acid conversion was recorded in the individual C16 acid HDO experiment (Figure 14a). The effect of the feed
composition on the C14 amine conversion was more pronounced than for the C16 acid. As with the C16 acid, the lowest C14 amine conversion, 37%, was recorded in the individual C14 amine HDN experiment. As the C16 acid content was increased, the C14 amine conversion started increasing, eventually reaching 73% at 80 mol % C16 acid. The difference in the reactivity was accompanied by a switch in selectivity, away from HDN and towards the formation of the C30 condensation products.

The relative ease of HDO compared to HDN can be observed from total yield of the C15 and C16 paraffins, which exceeded the C14 paraffin yield by approximately 10 percentage points throughout the range of studied feed compositions (Figure 14b). The sum of the C15 and C16 paraffin yields followed a similar trend as the C16 acid conversion, whereas the C14 paraffin yield remained stable, around 12%, throughout the studied feed composition range.

The nitrogen removal relative to the C14 amine conversion, which describes the HDN selectivity, or the fraction of the reacted C14 amine that underwent HDN, decreased linearly as the C16 acid content of the feed increased (Figure 14d). This reflects the simultaneously increasing C14 amine conversion and decreasing nitrogen removal. With 80 mol % of C16 acid in the feed, only 3% of the reacting C14 amine underwent HDN, compared to 45% in the individual C14 amine experiment.

The amount of condensation products remained stable for feed compositions that exceeded approximately 40 mol % of C16 acid (Figure 14d). An increasing share of the C14 amine was therefore consumed for the formation of the C30 amide and the C30 amine. In other words, the higher the initial C16 acid concentration was, the more the HDN of the C14 amine to the C14 paraffin was impeded by preferential condensation product formation.

5.3 The effect of the reaction conditions

The effect of the reaction temperature was studied by co-hydrotreating the C14 amine and C16 acid (80 ppm nitrogen, 80 ppm oxygen) at 270 °C, 300 °C and 330 °C and 80 bar H₂. An experiment at 0.39 g_cat/h/ g_reactants was carried out for each reaction temperature. A longer 0.88 g_cat/h/ g_reactants experiment was additionally done at 270 °C, while a shorter 0.13 g_cat/h/ g_reactants experiment was done at 330 °C, targeting similar conversion levels that were achieved in the 0.39 g_cat/h/ g_reactants activity test at 300 °C. The product distributions are presented in Figure 15.
Increasing the reaction temperature markedly increased the conversion and paraffin yield of both reactants at a given batch residence time (Figure 15) [I]. Furthermore, for a given conversion level, selectivity differences were observed between the different reaction temperatures. From the product distribution, nitrogen removal and the C14 amine conversion of the experiments carried out at 270, 300 and 330 °C, for batch residence times 0.88, 0.39 and 0.13 g_cat/h/g_reactants, respectively, it can be seen that the condensation product selectivity increased as the reaction temperature was decreased, while the paraffin selectivity increased with an increasing reaction temperature (Figure 15). Accordingly, the experiment at 270 °C gave the highest C14 amine conversion and the most C28 and C30 condensation products, but the lowest C14 paraffin yield and lowest nitrogen removal. The experiment at 330 °C, which had the lowest C14 amine conversion and the least C28 and C30 condensation products, had the highest paraffin yield and nitrogen removal.

Finally, co-hydrotreating experiments with the C14 amine and the C16 acid (80 ppm nitrogen, 80 ppm oxygen) were carried out at 300 °C with 60, 80 and 100 bar H₂ using a batch residence time of 0.39 g_cat/h/g_reactants. The experiments with 60 and 80 bar H₂ resulted in similar product distributions [I]. Meanwhile, the experiment with 100 bar H₂ gave paraffin yields that were a maximum of five percentage points higher. The H₂ pressure did therefore not have a marked effect on the activity at the studied reaction conditions.
6. The catalytic hydrotreatment of \(n\)-hexadecanamide

Primary amides are relevant model compounds for studying simultaneous HDN and HDO due to their presence in, e.g., algal and animal fat based feedstocks.\(^{19,20}\) In this work, the hydrotreatment of \(n\)-hexadecanamide (C16 amide) was studied on reduced, supported Pt, Ru, Rh, Pd, Ni, Co and Cu catalysts. The reaction network of the C16 amide is described on a general level in Section 6.1, while the influence of the active metal and support is discussed in Section 6.2. Section 6.3 presents the activity of the monometallic and bimetallic CeO\(_2\)-ZrO\(_2\) supported catalysts, which were synthesized based on the results of the studies on the effect of the active metal and the support.

6.1 Reaction network

The hydrotreatment of the C16 amide proceeded through several parallel and competing reaction pathways, most of which had been identified in the fatty acid and amine co-hydrotreating reaction experiments (Section 5) \([I]\). The activity and selectivity were highly dependent on the catalyst support \([II]\), the active metal \([III]\) and the combination thereof \([IV]\).

The reaction products of the C16 amide hydrotreating experiments comprised \(n\)-pentadecane (C15 paraffin), \(n\)-hexadecane (C16 paraffin), \(n\)-hexadecanal (C16 aldehyde), \(1\)-hexadecanol (C16 alcohol), palmitic acid (C16 acid), \(n\)-hexadecanitrile (C16 nitrile), \(1\)-hexadecylamine (C16 amine), dipentadecyl ketone (C31 ketone), \(n\)-hexadecyl hexadecylamine (C32 amine), palmityl palmitate (C32 ester) and \(n\)-hexadecyl hexadecanamide (C32 amide) \([II-IV]\). A reaction network is proposed in Scheme 1, based on the C16 amide experiments \([II-IV]\) and the findings of the C14 amine and C16 acid co-hydrotreating experiments \([I]\).
The catalytic hydrotreatment of n-hexadecanamide

Scheme 1. Proposed reaction network for the hydrotreatment of n-hexadecanamide (C16 amide). Indicated compounds: 1 C16 amide, 2 C32 isomide 3 C16 nitrile, 4 C16 acid, 5 C16 hemiaminal 6 C16 imine 7 C16 amine, 8 C16 aldehyde, 9 C16 alcohol, 10 C32 amide, 11 C32 amine, 12 C15 paraffin, 13 C16 paraffin, 14 C31 ketone, 15 C32 ester. The bimolecular deammoniation (BDA), direct dehydration (DHY), hydrogenation (HYD) and hydrolysis (HYDR) of the C16 amide, and the condensation (COND), hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) reactions of the intermediates have been indicated. The bimolecular ketonization of the C16 acid (KET) only occurred on the bare supports. Modified from Publication II with permission from the Royal Society of Chemistry.

The bare supports exhibited activity for the conversion of the C16 amide via two main pathways [II]. These pathways were the bimolecular deammoniation (BDA) of the C16 amide to an isoimide, which decomposed to the C16 nitrile and the C16 acid, and the dehydration of the C16 amide to the C16 nitrile (Scheme 1). The BDA pathway has been previously described by Davidson and Karten.76 The selectivity between the BDA and dehydration of the C16 amide depended on the support [II]. In addition to BDA and dehydration, the hydrolysis of the C16 amide to the C16 acid and ammonia may have occurred.62,75 Some bare supports exhibited activity for the bimolecular ketonization of the C16 acid to the C31 ketone, the reduction of the C16 acid to the C16 aldehyde, and further conversion of the C16 aldehyde to the C16 alcohol [II].38,90,91,126 The C16 aldehyde and the C31 ketone were not present in the product samples of the activity tests with the metal catalysts.

In the case of the supported metal catalysts, the initial conversion of the C16 amide may additionally have occurred via other pathways, including the HDN to the C16 aldehyde and the C16 alcohol, and the HDO to the C16 amine [II].29,59,63,66,71 The conversion of the C16 amide to the C16 alcohol and the C16 amine likely proceeded via a hemiaminal intermediate, as discussed in Section 2.1. Furthermore, based on the experimental data, the direct conversion of the C16 amide to the C15 paraffin could not be excluded on the Ru, Rh and Ni-containing catalysts [III, IV]. The imine, isomide and the hemiaminal
intermediates could not be detected from the product samples, and methane was the only C1 compound that was present in concentrations that exceeded the detection limit of the gas phase analysis [III]. The initial pathway selectivity for the conversion of the C16 amide could therefore not be unambiguously confirmed for the supported metal catalysts.

The C16 nitrile, the C16 acid, the C16 alcohol and the C16 amine were converted further on the metal catalysts, eventually forming the n-paraffins [II-IV]. The C16 nitrile was readily hydrogenated to the C16 amine, likely through the C16 imine, whereas the C16 acid was hydrogenated to the C16 alcohol, either directly or via the C16 aldehyde. Decarboxylation of the C16 acid and decarbonylation of the C16 aldehyde additionally occurred, producing the C15 paraffin. The C16 alcohol and C16 amine were converted to the C16 paraffin via C–O and C–N hydrogenolysis routes, or to the C15 paraffin via C–C bond cleavage pathways. Olefins were not detected from the product samples, but they may have been formed as intermediate products in the conversion of the C16 alcohol and the C16 amine to paraffins. The selectivity towards the C16 paraffin and the C15 paraffin strongly depended on the active metal [III].

The C32 condensation products were formed via multiple reaction pathways, analogously to the C14 amine and C16 acid co-hydrotreating experiments (Section 5) [I]. For example, the C32 amine could be formed by the HDO of the C32 amide, the condensation of the C16 alcohol and the C16 amine, the condensation and subsequent hydrogenation of the C16 aldehyde and the C16 amine, disproportionation of the C16 amine, and a reaction between the C16 imine and the C16 amine. The C32 amine was eventually converted to the C16 paraffin or the C15 paraffin, with a selectivity depending on the active metal.21,85,101

6.2 The influence of the support and the active metal

6.2.1 Activity of the bare oxide supports

The bare supports exhibited activity for the conversion of the C16 amide to the C16 nitrile and C16 acid, and in some cases, for the further conversion of the C16 acid to the C16 aldehyde, C16 alcohol and the C31 ketone (Scheme 1) [II]. The presence of an active metal was, nevertheless, required for significant formation of paraffins and hydrogenated intermediate products.

Figure 16 presents the product distribution and the nitrogen removal from the activity tests on the bare supports at 300 °C and 80 bar H2, using 100 ppm nitrogen in the feed and a reaction time of 60 min. The product distribution of a thermal test carried out in similar conditions is included, additionally. The bare supports have been grouped according to the strength of their Lewis acid sites. As described in Section 4.1, the Si-Al group contains the supports with the strongest Lewis acid sites (30SiO2-70Al2O3, 5SiO2-95Al2O3, γ-Al2O3), while the Ti-Nb group comprises the supports with intermediate strength Lewis acid sites.
(TiO$_2$, Nb$_2$O$_5$) and the Ce-Zr group comprises the materials with weak Lewis acid sites (ZrO$_2$, CeO$_2$-ZrO$_2$). The non-acidic SiO$_2$ support forms the Si group.

The materials have been grouped according to the strength of their Lewis acid sites. The data is from Publication II.

The bare supports of the Si-Al group were active for the initial conversion of the C16 amide via BDA, as indicated by the stoichiometric formation of the C16 acid and the C16 nitrile (Scheme 1, Figure 16) [II]. The bare supports of the Ce-Zr group likewise seemed to favor the initial conversion of the C16 amide through BDA, but also exhibited activity for converting the C16 acid further to the C16 aldehyde, C16 alcohol and the C31 ketone. Both the reduction of the C16 acid to the C16 aldehyde and the bimolecular ketonization of the C16 acid to the C31 ketone have been proposed to be Lewis acid catalyzed.

The BDA and dehydration of the C16 amide occurred thermally, but with a considerably lower activity than on the tested bare supports, except for SiO$_2$ (Figure 16). The poor activity of the bare SiO$_2$ support may have been due to the lack of acid sites (Table 5). The nitrogen removal and conversion were likely overestimated for the thermal test and the activity test with the bare SiO$_2$ support, due to precipitation of the model compound, which complicated the product recovery.

In contrast to the other groups, the bare supports of the Ti-Nb group preferred the dehydration of the C16 amide to the C16 nitrile, as suggested by the high (>60%) yields of the C16 nitrile, and low (<10%) yields of the C16 acid and C16 acid derivatives (Figure 16). Shimizu et al. discovered that the Lewis acid sites of Nb$_2$O$_5$ and MoO$_x$/TiO$_2$ interacted strongly with the carbonyl group of
acetamide. The interaction strength between the amide carbonyl group and the Lewis acid sites of the support correlated with the catalytic activity of the corresponding supported Pt catalysts for the HDO of amides to amines.\textsuperscript{59} Considering this observation, it is likely that the intermediate strength Lewis acid sites of TiO\textsubscript{2} and Nb\textsubscript{2}O\textsubscript{5} (Figure 8) catalyzed the dehydration of the C16 amide to the C16 nitrile.

6.2.2 Activity of the supported metal catalysts

The active metal enhanced the conversion, nitrogen removal and oxygen removal of the supported metal catalysts relative to the bare supports, and introduced activity for the hydrogenation and hydrolysis reactions in the reaction network (Scheme 1). Figure 17 displays the product distribution, conversion, nitrogen removal and oxygen removal of the supported metal catalysts in the hydrotreatment of the C16 amide at 300 °C and 80 bar H\textsubscript{2}, using an initial nitrogen content of 100 ppm and a reaction time of 60 min.

![Figure 17. Product distribution, conversion (×), nitrogen removal (○) and oxygen removal (□) of the Pt catalysts supported on different oxides and the Ru, Rh, Pd and Ni catalysts supported on ZrO\textsubscript{2}, in the hydrotreatment of the C16 amide (300 °C, 80 bar H\textsubscript{2}, 60 min). The catalysts have been grouped according to the strength of their Lewis acid sites. The nitrogen removal was obtained from the total nitrogen content analysis, while the oxygen removal was derived from the GC analysis. The data is from Publications II and III.](image)

The product distribution of the Pt/\γ-Al\textsubscript{2}O\textsubscript{3} (a), Pt/TiO\textsubscript{2} (b), Pt/ZrO\textsubscript{2} (c) and Ru/ZrO\textsubscript{2} (d) catalysts in the hydrotreatment of the C16 amide at 300 °C and 80 bar H\textsubscript{2} is presented as a function of batch residence time in Figure 18. Pt/\γ-Al\textsubscript{2}O\textsubscript{3} is representative of the Si-Al group, while Pt/TiO\textsubscript{2} represents the Ti-Nb group. The Pt/ZrO\textsubscript{2} and Ru/ZrO\textsubscript{2} catalysts represent the Ce-Zr group. The
The catalytic hydrotreatment of n-hexadecanamide

60 min experiments of Figure 17 correspond to a batch residence time of 0.37 g\textsubscript{cat}/h/g\textsubscript{amide}.

![Graphs showing product yields vs. batch residence time for different catalysts](image)

**Figure 18.** Product distribution of (a) Pt/γ-Al\textsubscript{2}O\textsubscript{3} (Si-Al), (b) Pt/TiO\textsubscript{2} (Ti-Nb), (c) Pt/ZrO\textsubscript{2} (Ce-Zr), and (d) Ru/ZrO\textsubscript{2} (Ce-Zr) as a function of batch residence time in the hydrotreatment of the C16 amide at 300 °C and 80 bar H\textsubscript{2} [II-III]. The 60 min reference experiments of Figure 13 correspond to a batch residence time of 0.37 g\textsubscript{cat}/h/g\textsubscript{amide}. The trendlines have been added to guide the eye.

The supported metal catalysts differed in their preference towards the initial C16 amine conversion route and in the activity and selectivity for the formation of C32 condensation products and the C15 and C16 n-paraffins out of the intermediate products (Figure 17, Figure 18) [II, III]. This was reflected in both the C16 amide conversion, oxygen removal and nitrogen removal on the catalysts.

Based on the characterization data presented in Section 4.1, the differences in the activity of the supported Pt catalysts could be attributed to the properties of the support [II]. Meanwhile, the differences between the ZrO\textsubscript{2}–supported Pt, Pd, Ru and Rh catalysts mainly appeared to be related to the metal identity and its influence on the adsorption strength and adsorption mode of the reactants and intermediate products [III]. However, in the case of Ni/ZrO\textsubscript{2}, the low dispersion (Table 5) and poor reducibility of Ni (Figure 7) likely impeded the catalytic activity.

The following paragraphs discuss the influence of the active metal and the support on the activity for the hydrotreatment of the C16 amide. The initial C16 amide conversion route, the activity for the conversion of the oxygen-containing intermediate products, the activity for the conversion of the nitrogen-containing intermediate products, and the formation and decomposition of the C32...
condensation products, are addressed separately, due to the complexity of the reaction network (Scheme 1).

The initial C16 amide conversion route

The support significantly influenced the initial C16 amide conversion route, and thus determined the distribution between the oxygen-containing and nitrogen-containing intermediate products [II]. The supported Pt catalysts of the Ti-Nb group strongly favored the initial oxygen removal of the C16 amide, which was reflected in exceptionally high yields of the nitrogen containing intermediate products compared to the other catalysts (Figure 17, Figure 18). For example, the C32 amine yields on the supported Pt catalysts of the Ti-Nb group were more than 20 percentage points higher compared to the other catalysts in the 60 min reference experiments. The C16 nitrile was the dominant product during the earliest batch residence time points in the time series experiments (Figure 18b), which suggests that the Lewis acid catalyzed dehydration of the C16 amide to the C16 nitrile was the favored initial conversion route, similarly to the bare supports (Figure 16). The direct HDO of the C16 amide to the C16 amine (Scheme 1) may have occurred in parallel.

The catalysts of the groups Si, Si-Al and Ce-Zr initially converted the C16 amide to oxygen-containing and nitrogen-containing intermediate products with a rather similar selectivity (Figure 17, Figure 18), analogously to the respective bare supports (Figure 16) [II]. Given the presence of the C16 acid and the C16 nitrile in the product samples and considering the reactivity of the C16 acid (Section 5), it is possible that the BDA pathway (Scheme 1) remained a prominent C16 amide conversion route on the supported metal catalysts, as on the bare supports. This is supported by the similar C16 amide conversion levels (59-69%) on the bare ZrO2 and the Ru/ZrO2, Rh/ZrO2, Pd/ZrO2 and Ni/ZrO2 catalysts [III]. The similarity of the product distribution (Figure 17) and nitrogen removal (28-31%) on the bare ZrO2 support and the Pd/ZrO2 and Ni/ZrO2 catalysts is also noteworthy.

The C16 amine and the C16 alcohol were the most important intermediate products on the supported Pt catalysts of the groups Si-Al and Ce-Zr (Figure 17, Figure 18). For example, in the batch residence time series on Pt/ZrO2, yields up to 23% were recorded for both the C16 amine and the C16 alcohol (Figure 18c). The C16 amine and the C16 alcohol were also readily present in the product samples corresponding to the earliest studied batch residence time points. It is therefore likely that the supported metal catalysts catalyzed the direct conversion of the C16 amide to the C16 amine and the C16 alcohol via the hemiaminal route (Scheme 1), in addition to the further conversion of the support-derived intermediates, i.e., the hydrogenation of the C16 nitrile to the C16 amine and the reduction of the C16 acid to the C16 aldehyde and the C16 alcohol.62,67

As discussed in Section 2.1, the hemiaminal intermediate may have been formed via adsorption and activation of the carbonyl group of the C16 amide on the Lewis acid sites of the support, followed by hydrogenation on the active metal.62,67 The decomposition of the hemiaminal, in turn, may have been metal-catalyzed.61 The poor conversion on Pt/SiO2 (Figure 17) could therefore be
explained with the absence of Lewis acid sites hindering the hemiaminal formation (Table 5). The enhanced C16 amide conversion on the supported Pt catalysts of the Ce-Zr group compared to the Si-Al group may have been due to the weak Lewis acid sites of the Ce-Zr group (Figure 8) facilitating the formation of the hemiaminal. Meanwhile, the higher C16 amide conversion on Pt/ZrO₂ compared to Ru/ZrO₂, Rh/ZrO₂, Pd/ZrO₂ and Ni/ZrO₂ (Figure 17), could hint that Pt was more active than the other metals for the hydrogenation C16 amide to the hemiaminal.

Considering the high C15 paraffin yields on the Ru/ZrO₂ and Rh/ZrO₂ catalysts (Figure 17, Figure 18d), the direct conversion of the C16 amide to the C15 paraffin cannot be excluded based on the experimental data. For example, the C15 paraffin yield on Ru/ZrO₂ was 17% at batch residence time point 0.09 gcat/h/g_amide, while the yields of the other products were below 3% each. The formation of Cₙ₋₁ paraffins from Cₙ fatty acids has, analogously, been proposed to occur through the splitting of a formic acid species over supported Pd catalysts.\(^7,13\)\(^0\) Computational studies on the hydrotreatment of long-chain amides on different metals could shed light on the possible reaction mechanism.

The conversion of the oxygen-containing intermediate products

Both the active metal and the support influenced the activity for the conversion of the oxygen-containing intermediate products to the C15 and C16 paraffins (Figure 17, Figure 18) [II, III]. The decarbonylation of the C16 aldehyde, the decarboxylation of the C16 acid to the C15 paraffin, and the hydrogenation of the C16 acid and C16 aldehyde to the C16 alcohol, were catalyzed by the metal sites.\(^11\),\(^18\),\(^12\),\(^7\),\(^13\)

The supported Pt catalysts favored the hydrogenation of the C16 acid and the C16 aldehyde to the C16 alcohol, and the subsequent conversion of the C16 alcohol to the C16 paraffin (Scheme 1, Figure 17, Figure 18). The C15 paraffin yield did not exceed 15% for the supported Pt catalysts at the highest studied batch residence time (1.85 gcat/h/g_amide), while the C16 paraffin yields ranged between 39 and 77%. No correlation between the support or the Pt-related properties and the C15 paraffin yield was identified [II].

The Ru/ZrO₂, Rh/ZrO₂, Pd/ZrO₂ and Ni/ZrO₂ catalysts, in turn, favored the decarboxylation and decarbonylation routes, which was reflected in the preferential formation of the C15 paraffin (Figure 17) [III]. It is possible that the C16 alcohol could be converted to the C15 paraffin on these metals as well, via dehydrogenation of the C16 alcohol to the C16 aldehyde, followed by decarbonylation.\(^8\),\(^5\),\(^8\) Considering the findings of the C16 acid and C14 amine co-hydrotreating experiments (Section 5) and the batch residence time series on the different supported Pt catalysts (Figure 18), this pathway was not favored by Pt in the studied reaction conditions. The metal identity was thus decisive for the selectivity for the C15 paraffin and the C16 paraffin.

The influence of the support on the activity towards the HDO of the oxygen-containing intermediate products was reflected in, e.g., the evolution of the C16 acid and the C16 alcohol yields on the supported Pt catalysts of the groups Si-Al and Ce-Zr (Figure 17, Figure 18) [III]. The supported Pt catalysts of the Ce-Zr
The catalytic hydrotreatment of n-hexadecanamide group converted the oxygen-containing intermediate products more efficiently than the supported Pt catalysts of the Si-Al group.

The conversion of the C16 acid to the C16 alcohol may have proceeded via the adsorption of the C16 acid on the Lewis acid sites of the supports and hydrogenolysis catalyzed by Pt. The HDO of the C16 alcohol to the C16 paraffin may have proceeded analogously, or through dehydration via an E2 mechanism involving Lewis acid-base site pairs and hydrogenation catalyzed by Pt. The dehydration of the C16 alcohol may, alternatively, have been catalyzed by Brønsted acid sites.

The HDO activity of the supported Pt catalysts of the Ce-Zr group was likely related to their weak Lewis acid sites (Figure 8). These Lewis acid sites can be e.g., incompletely coordinated Zr or Ce cations. Based on the overall product distribution, conversion, oxygen removal and nitrogen removal, the Pt/25CeO$_2$-75ZrO$_2$ catalyst was more active than Pt/ZrO$_2$ (Figure 17). This could be due to the properties of the support, as the 25CeO$_2$-75ZrO$_2$ support was readily reducible (Figure 7) and had a higher concentration of Lewis acid sites than ZrO$_2$ (Table 5).

The supported Pt catalysts of the Ti-Nb group gave lower yields of the oxygen-containing intermediate products than the supported Pt catalysts of the other groups (Figure 17). This was due to the activity of the intermediate strength Lewis acid sites for the dehydration of the C16 amide to the C16 nitrile (Figure 16). The conversion of the oxygen-containing intermediate products was complete by point 0.75 g$_{cat}$/g$_{amide}$ in the batch residence time series on Pt/TiO$_2$ (Figure 18).

The conversion of the nitrogen-containing intermediate products
The C16 nitrile, the C16 amine and the C32 amine were the most important nitrogen-containing intermediate products in the C16 amide reaction network (Figure 17, Scheme 1). In this section, the conversion of the C16 nitrile and the C16 amine are discussed.

The C16 nitrile was readily hydrogenated to the C16 amine (Scheme 1) on the supported metal catalysts, and the reaction was catalyzed by the active metal. Particularly the supported Pt catalysts exhibited a high activity towards the reaction (Figure 17, Figure 18).

Separate hydrotreating experiments were carried out for the ZrO$_2$-supported metal catalysts, using the C16 amine as a model compound, to assess the HDN activity of the catalysts without the interference of simultaneous HDO [III]. The active metal had a pronounced effect on the activity and selectivity, as illustrated in Figure 19, where the product distribution and nitrogen removal of the C16 amine HDN experiments are presented. The experiments were carried out at
300 °C, 80 bar H₂ for 60 min, using an initial nitrogen content of 100 ppm, similarly to the C16 amide experiments of Figure 17.

**Figure 19.** Product distribution and nitrogen removal (○) of the ZrO₂-supported metal catalysts in the hydrotreatment of the C16 amine. Reaction conditions: 300 °C, 80 bar H₂, 60 min, 100 ppm nitrogen. Reproduced from Publication III (licensed under CC BY 4.0).

The nitrogen removal of the catalysts was 8–30 percentage points lower in the C16 amine hydrotreating experiments (Figure 19) than in the C16 amide hydrotreating experiments (Figure 17). Furthermore, the bare ZrO₂ support did not exhibit any significant activity for the conversion of the C16 amine, whereas a nitrogen removal of 28% was obtained on the bare ZrO₂ in the hydrotreatment of the C16 amide (Figure 16). These findings emphasize the contribution of the BDA route and the activity of the support for the BDA reaction, in the hydrotreatment of the C16 amide (Scheme 1).

Three nitrogen removal routes were identified in the C16 amine HDN experiments on the ZrO₂-supported metal catalysts, and the selectivity between these depended on the active metal [III]. The C16 amine could undergo C–N bond hydrogenolysis to form the C16 paraffin, C–C bond cleavage to form the C15 paraffin, and disproportionate to form the C32 amine (Scheme 1). The C–C bond cleavage of the C16 amine to the C15 paraffin was the dominant nitrogen removal route on Ru/ZrO₂ and Rh/ZrO₂ (Figure 19). Pt/ZrO₂ readily produced the C16 paraffin and the C32 amine and did not exhibit significant activity for the C–C bond cleavage of the C16 amine. The Pd/ZrO₂ and Ni/ZrO₂ catalysts favored the disproportionation of the C16 amine to the C32 amine and only formed traces of the paraffins, which aligns with the observations of the C16 amide experiments on these catalysts (Figure 17). The other C32 amine formation pathways and the HDN of the C32 amine will be discussed further in the next section.

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As noted in Section 2.3, the three C16 amine HDN pathways may have been initiated by the dissociative adsorption of the C16 amine on the metal sites as a hydrogen-deficient surface intermediate, $\text{C}_{16}\text{H}_{33}\text{CH}_{x}\text{NH}_y$. The active metal influences the adsorption strength, adsorption mode, and the transition states in the reaction mechanism, which in turn can explain the differences in the activity and selectivity towards the different reaction pathways.

The C–C bond cleavage of alkyl amines only has been sparsely reported in literature before, and the mechanism is not fully understood. Based on computational studies on the adsorption and HDO of alcohols on reduced metals, it is possible that the initial hydrogen cleavage channel in the dissociative adsorption of the C16 amine, which can occur either from the amine group or α-carbon, influenced the selectivity between the C–C and C–N bond cleavage routes on the different metals.

The active metal also affects the hydrogen content of the adsorbed species that undergoes C–N or C–C bond cleavage. For example, Ru has been suggested to cleave both hydrogen atoms of the amine group prior to the C–N bond cleavage step, while Pt and Pd may retain both hydrogen atoms.

The activity for both C–C and C–N bond cleavage decreases from left to right in the periodic table for the reduced metals of groups 8-11. While the amine group affects the reactivity of the adjacent C–C bond, the periodic trend for the activity of reduced metals for C–C bond cleavage was reflected in the product distribution of the C16 amine experiments (Figure 19). In contrast, the periodic trend for the activity towards C–N bond cleavage only held for Pt/ZrO$_2$ and Pd/ZrO$_2$. This could indicate that the relative ability of the metals to activate CH$_x$ species influenced the preference between C–C and C–N bond cleavage, analogously to what has been found in the hydrotreatment of alcohols. Computational studies on the HDN of alkyl amines would be useful to clarify the reaction mechanisms.

Similarly to the HDO of the C16 alcohol, it may be possible that the HDN of the C16 amine, additionally, proceeded via a mechanism involving the adsorption of the C16 amine to a Lewis acid site and hydrogenolysis catalyzed by the metal sites. The HDN of amines can also proceed via the Brönsted acid site catalyzed Hofmann elimination to an olefin and ammonia, followed by hydrogenation of the olefin on the metal sites. Considering the absence of Brønsted acid sites on most catalysts (Table 5) and the relatively similar nitrogen removal on the different supported Pt catalysts (Figure 17), this was likely not a major reaction pathway.

The catalyst support had a less pronounced effect than the active metal on the HDN activity in the hydrotreatment of the C16 amide (Figure 17, Figure 18). The HDN of the nitrogen-containing intermediate products was, nevertheless, influenced by the presence of the oxygen-containing intermediate products [I], which in turn depended on the support [II]. In the complex C16 amide hydrotreating reaction network, the direct effect of the support on activity for the HDN of the nitrogen-containing intermediate products therefore appeared
to be outweighed by the effect of the support on the initial C16 amide conversion route and on the HDO activity [II].

**The formation and decomposition of the C32 condensation products**

The C32 condensation products were readily formed on the Pt, Pd and Ni catalysts, but their formation was limited on Ru and Rh (Figure 17, Figure 18) [II, III]. The preference towards the formation of the C32 amide and C32 amine thus depended on the active metal, but was also influenced by the presence of the oxygen-containing and the nitrogen-containing intermediate products, which in turn were influenced by the catalyst support, as described in the previous sections.

In the case of the supported Pt catalysts, the highest amounts of the C32 amine were formed over the Ti-Nb group (Figure 17) [II]. This may have followed from the high intermediate concentrations of the C16 nitrile and C16 amine. Pt is, indeed, known to exhibit considerable activity for the formation of secondary amines via disproportionation of primary amines and the condensation of imines and primary amines (Scheme 1).\(^{96,48,120,144,145,138,146}\) The C32 amine was likewise readily obtained on the supported Pt catalysts of the Ce-Zr group, but its formation through condensation of the C16 alcohol and the C16 amine was favorable, as a result of the significant intermediate C16 alcohol yields [I].\(^{128,147}\) The formation of the C32 amide can be catalyzed by Pt sites only, but a mechanism involving both Pt and the Lewis acid sites of the support may have been possible additionally, particularly for the pathways that involved C–O bond cleavage (Scheme 1).\(^{97,146,48,148,43}\)

The C32 amide was readily formed on the supported Pt catalysts of the Si-Al group (Figure 17). The C32 amide was formed through condensation of the C16 acid and the C16 amine and the reaction could be catalyzed by the Lewis or Brønsted acid sites of the bare supports [I]. Based on the observations of the C16 acid and C14 amine co-hydro treating experiments with the different feed compositions (Section 5.2), it is likely that the high C32 amide yield of the Si-Al group followed from the relatively high concentrations of the C16 acid in the reaction mixture. The high C16 acid concentrations compared to the other catalysts, in turn, reflect the poor HDO activity of the group.

The decomposition of the C32 compounds eventually accounted for a significant share of the C16 paraffin yield on the supported Pt catalysts. The HDO of the C32 amide to the C32 amine was catalyzed by Lewis acid sites and Pt sites.\(^{48,59,101,105,149}\) The C32 amide was converted more efficiently on the groups Ce-Zr and Ti-Nb than on the Si-Al group (Figure 18), which may be related to the Lewis acid site strength (Figure 8).

The decomposition of C32 amine may have involved the dissociative adsorption of the C32 amine to an alkyl and amine fragment on the Pt sites, as described by Sivasankar and Prins.\(^{101}\) Based on the batch residence time series experiments, the HDN of the C32 amine did not seem to occur readily until the oxygen-containing intermediates had been converted (Figure 18), which may suggest that the presence of the oxygen-containing compounds inhibited the reaction [I]. The HDN of the C32 amine thus occurred more readily on the groups Ti-Nb and Ce-Zr compared to the Si-Al group, which was reflected in the
The catalytic hydrotreatment of n-hexadecanamide

slow evolution of the C16 paraffin yield and accumulation of the C32 compounds on Pt/γ-Al₂O₃ compared to Pt/ZrO₂ and Pt/TiO₂ (Figure 18).

To summarize, the acid and redox properties of the support influenced the selectivity for the initial C16 amide conversion route, and for the activity towards the HDO of the oxygen containing intermediate products [II]. These, in turn, influenced the condensation reaction pathway preference [I, II]. The metal properties were decisive for the activity and selectivity towards the C–C, C–O and C–N bond cleavage routes in the conversion of the intermediate products to the paraffins, and for the condensation reaction selectivity [III].

6.3 Ceria-zirconia supported monometallic and bimetallic catalysts

Bimetallic catalysts can exhibit an enhanced activity, selectivity and stability compared to corresponding monometallic systems.⁴⁹,¹⁵⁰ This can be due to, e.g., electronic interactions between the active metals, which promote the adsorption and activation of reactants⁵⁵, the generation of new active sites⁵³ and synergistic effects, where the individual metals catalyze different elementary steps⁵⁶. The activity of bimetallic catalysts has been demonstrated in HDO reactions⁵²–⁵⁸ and in the hydrogenation of nitriles and amides to amines,⁶⁰,⁶⁷,⁷⁴,¹²² which suggests that they could be an interesting option for the HDO and HDN of primary amides to n-paraffins.

A series of 17CeO₂–83ZrO₂ supported bimetallic and monometallic catalysts (Section 4.2) was tested for their activity in the hydrotreatment of the C16 amide, in order to investigate bimetallic effects and whether a catalyst with a higher activity than the monometallic supported Pt catalysts and the ZrO₂ supported metal catalysts (Section 6.2) could be obtained. A further motivation behind the study was to evaluate if pairing a noble metal with a cheaper base metal and a suitable support allows for decreasing the noble metal loading, without compromising the activity.

Figure 20 displays the product distribution, nitrogen removal and oxygen removal of the C16 amide hydrotreating experiments on the bimetallic and monometallic catalysts supported on 17CeO₂–83ZrO₂. The experiments were carried out at 300 °C, 80 bar H₂ for 60 min, using an initial nitrogen content of 100 ppm.
The catalytic hydrotreatment of n-hexadecanamide

Figure 20. Product distribution, conversion (×), oxygen removal (□) and nitrogen removal (○) of the monometallic and bimetallic catalysts supported on 17CeO₂–83ZrO₂ in the hydrotreatment of the C16 amide (100 ppm nitrogen). The nitrogen removal was obtained from the total nitrogen content analysis, while the oxygen removal was derived from the GC analysis. Reaction conditions: 300 °C, 80 bar H₂, 60 min. Modified from Publication IV (licensed under CC BY 4.0).

The monometallic and bimetallic catalysts exhibited remarkably different catalytic properties (Figure 20) [IV]. This was reflected in a significant variability in the nitrogen removal (30-76%), oxygen removal (50-90%), total paraffin yield (1-69%), C32 compound yield (2-17%) and in the preference between the C15 and the C16 paraffins.

The product distribution of the bimetallic catalysts differed from the sum or mean of the corresponding monometallic catalysts. This is further highlighted in Figure 21, where the product distributions of the Pt (a), PtCo (b), Co (c), Ni (d), RuNi (e), Ru (f) and PtNi (g) catalysts are presented as a function of batch residence time. The Cu-containing catalysts exhibited a poor hydrogenolysis and hydrogenation activity and were therefore not studied further [IV].
The catalytic hydrotreatment of n-hexadecanamide

Figure 21. Product distribution for the hydrotreatment of the C16 amide at 300 °C and 80 bar H₂ as a function of batch residence time for the 17CeO₂-83ZrO₂ supported (a) Pt, (b) PtCo, (c) Co, (d) Ni, (e) RuNi, (f) Ru and (g) PtNi catalysts. The 60 min reference experiments of Figure 16 correspond to a batch residence time of 0.37 gₐₙₜ/ gₐ₅ₚₐ₅ sınₜ. The lines have been added to guide the eye. Reproduced from Publication IV (licensed under CC BY 4.0).

Similar overall trends were identified from the product distribution of the 17CeO₂-83ZrO₂ supported bimetallic catalysts (Figure 20, Figure 21) and the product distribution of the supported Pt catalysts and the ZrO₂-supported metal catalysts (Figure 17, Figure 18). As described in Section 6.2, the support influenced the initial C16 amide conversion pathway, while the active metals dictated the selectivity for condensation reactions and for C–C, C–N and C–O bond cleavage routes in the formation of the paraffins. HDO proceeded more efficiently than HDN, and the C16 and C32 amines were the last intermediate products to be converted on the studied catalysts. The activity of the PtNi and RuNi catalysts was, nevertheless, considerably higher compared to the monometallic supported Pt catalysts and the ZrO₂-supported metal catalysts.

It is noteworthy, that the monometallic 0.5 wt. % Ru/17CeO₂-83ZrO₂ and 1.5 wt. % Ni/17CeO₂-83ZrO₂ catalysts (Figure 20) showed a high conversion and nitrogen removal compared to the monometallic 1 wt. % Ru/ZrO₂ and 1 wt. % Ni/ZrO₂ catalysts (Figure 17). Even taking the increased Ni loading into account, the observation suggests that the enhancing effect of the reducible 17CeO₂-83ZrO₂ support also applied for other active metals than Pt. The following paragraphs give an overview of the activity and product distribution of the monometallic and bimetallic catalysts.

The monometallic Pt catalyst favored the formation of the C16 paraffin via hydrogenolysis of the C16 and C32 intermediate products [I-IV], while the low-
activity monometallic Co catalyst gave over 50% of the C32 amine, and only formed traces of the paraffins (Figure 21). The PtCo catalyst, in turn, showed activity for the formation of the C15 paraffin from the C16 amine and the C16 alcohol, which was not observed on the monometallic Pt and Co catalysts. While the product distribution of the PtCo catalyst deviated from the monometallic counterparts significantly, it is noteworthy that the total paraffin yield of PtCo did not exceed the total paraffin yield of the monometallic Pt catalysts at batch residence times higher than 0.75 g cat/h/amide.

The monometallic Ni catalyst formed the C15 paraffin via C–C bond cleavage routes of the C16 amine, the C16 alcohol and the C32 amine (Figure 21d) [IV]. Mechanistically, the Ni catalyst thus appeared to deviate from the Rh and Ru catalysts (Figure 17), which did not accumulate the C16 and C32 intermediate products [III]. The activity of the PtNi catalyst significantly exceeded the activity of both the monometallic Pt and Ni catalysts, but the product distribution was similar to the monometallic Ni. Out of the catalysts studied in this thesis, the different monometallic Pt catalysts (Figure 17, Figure 21a) were therefore the only materials which were more selective for the formation of the C16 paraffin than the C15 paraffin.

The RuNi catalyst showed the highest activity for the formation of the C15 paraffin out of the studied catalysts, while the C32 amine yield was below 2% throughout the studied range of batch residence times (Figure 21e). The C15 paraffin yield was anticipated, considering the product distribution of the monometallic Ru and Ni catalysts. The low C32 amine yield, on the other hand, was remarkable, given the tendency of the Ni catalyst for the formation of the C32 amine (Figure 19, Figure 21d).

Based on the catalyst characterization by H₂-TPR and XPS (Section 4.2), it is possible that the differences in the catalytic properties of the bimetallic and their respective monometallic catalysts followed from electronic interactions between the metals and, potentially, an enhanced reducibility of the base metal [IV]. Furthermore, a correlation was identified between both the CO adsorption capacity and Lewis acid site concentration of the catalysts and the paraffin yield, as displayed in Figure 22. Indeed, both metal sites and Lewis acid sites of the support have been proposed to be mechanistically involved in the hydrogenolysis mechanisms, and the Lewis acid sites that are located near the perimeter of the metal particles have been suggested to be critical for the activity. There was also a positive correlation between the CO adsorption capacity and nitrogen removal. The increased activity of the RuNi and PtNi catalysts relative to the monometallic Ru and Pt catalysts, respectively, may thus additionally have been due to an increased number of surface metal sites and Lewis acid sites [IV]. On the other hand, a relatively low number of surface metal sites and Lewis acid sites may explain why the activity of the PtCo catalyst did not markedly exceed the activity of the monometallic Pt catalyst, despite the synergistic effects between the active metals (Figure 21a-c). For the RuNi, PtNi and Ni catalysts, a contribution of the Brønsted acid sites (Table 6) or strong basic sites (Figure 11) on the activity is also possible.
Overall, the activity tests emphasized the potential of bimetallic catalysts in the HDN and HDO of the C16 amide to n-paraffins. Pairing Ni with a noble metal and a reducible support gave highly active catalysts, which outperformed all of the monometallic noble metal catalysts that were presented in Section 6.2.2 in terms of nitrogen removal and paraffin yield, despite a lower noble metal loading (Figure 17, Figure 20).

The purpose of this thesis was to understand the influence of the catalyst composition on the activity and selectivity for the hydrotreatment of amides to n-paraffins, and to identify active catalyst compositions for the reaction. This was achieved via studies on the effect of the support and the active metal, and by the synthesis of the bimetallic RuNi/CeO$_2$-ZrO$_2$ and PtNi/CeO$_2$-ZrO$_2$ catalysts, respectively.
7. Conclusions and outlook

The production of renewable fuels via the hydrotreatment of bio-based feedstocks enables mitigating the CO$_2$ emissions of the transport sector. In this thesis, the activity of supported noble and base metal catalysts for simultaneous and competitive HDO and HDN reactions were studied in the hydrotreatment of fatty amides and their derivatives.

Competitive HDN and HDO reactions were studied by co-hydrotreating the C14 amine (1-tetradecylamine) and the C16 acid (palmitic acid) over a Pt/ZrO$_2$ catalyst. As indicated by a higher conversion and paraffin yield, the C16 acid was more reactive than the C14 amine, both when the compounds were hydrotreated separately and together. The HDN of the C14 amine was inhibited by the HDO of the oxygen-containing compounds and by the preferential formation of condensation products. The condensation reactions became increasingly favorable when the oxygen content of the feed was increased, which was reflected in a linearly decreasing HDN selectivity. The secondary amines and amides decomposed to $n$-paraffins at longer batch residence times, when the more reactive oxygen-containing compounds had been consumed, eventually accounting for a significant share of the formed paraffins. Increasing the reaction temperature favored the formation of paraffins, while decreasing the reaction temperature promoted the condensation reactions.

The hydrotreatment of the C16 amide (n-hexadecanamide) was studied over a series of Pt catalysts supported on different oxides, and on different metals supported on ZrO$_2$. A reaction network for the HDN and HDO of the C16 amide was formulated based on the product distribution of the catalytic activity tests on the various supports and supported metal catalysts.

The catalyst composition had a pronounced effect on the activity and selectivity in the hydrotreatment of the C16 amide. The Lewis acid properties of the support dictated the initial C16 amide conversion route and influenced the activity towards the HDO of the oxygen-containing intermediate products. For example, the intermediate strength Lewis acid sites on TiO$_2$ and Nb$_2$O$_5$ were highly active for the dehydration of the C16 amide to the C16 nitrile, whereas the other materials initially converted the C16 amide to oxygen-containing and nitrogen-containing intermediate products with a similar selectivity. The HDO of the oxygen containing intermediate products proceeded particularly efficiently on the catalysts supported on CeO$_2$-ZrO$_2$, which could be attributed to the weak Lewis acid sites on the support. The differences in the HDN activity between the Pt catalysts on the different supports were more subtle than the
differences in the HDO activity, due to the mechanistic involvement of the Lewis acid sites of the support in several of the HDO reactions.

The active metal had a pronounced effect on both the HDN and HDO activity. The active metal influenced the selectivity for condensation reactions, and for the C–N, C–O and C–C bond cleavage routes in the formation of paraffins, thus dictating the distribution between the C15 and C16 paraffins and the C32 condensation products. The condensation reactions were favored on the Pt, Pd and Ni-based catalysts, but mitigated on Ru and Rh. Out of the active metals, only Pt favored the formation of the C16 paraffin from both the oxygen-containing and nitrogen-containing products. In line with the observations of the C14 amine and C16 acid co-hydrotreating experiments, the HDO activity exceeded the HDN activity on the tested catalysts, and the C16 and C32 amines were the last intermediate products to be converted in the C16 amide hydrotreating reaction network.

Finally, the activity of a series of CeO$_2$-ZrO$_2$ supported bimetallic catalysts was evaluated in the hydrotreatment of the C16 amide. The product distribution of the bimetallic catalysts differed from the corresponding monometallic catalysts markedly, which, considering the catalyst characterization data obtained from H$_2$-TPR, XPS, CO pulse titration and pyridine FTIR measurements, could be attributed to interactions between the active metals and an increased number of surface metal and Lewis acid sites. The combination of Ni with a noble metal was highly beneficial for the activity in the HDO and HDN of the C16 amide. The bimetallic RuNi/CeO$_2$-ZrO$_2$ catalyst showed the highest activity and selectivity towards the formation of the C15 paraffin out of the catalysts tested in this work, with only limited formation of the C32 compounds.

The purpose of this work was to gain an understanding on the activity, selectivity and reaction network of different reduced metal catalysts in the hydrotreatment of fatty amides. In order to assess the potential of reduced metal catalysts for larger scale application, conducting deactivation studies and test runs with real feeds would, however, be necessary. Particularly, the tolerance to impurities, such as H$_2$S, should be investigated. Considering the complexity of the reaction network, kinetic studies would be beneficial to clarify the importance of the individual reaction pathways on the different catalysts, while DFT studies could bring mechanistic insights, particularly related to the nitrogen removal pathways. In terms of further catalyst development, focusing on a specific catalyst system and investigating, e.g., the effect of the active metal loading, dispersion and distribution, and the effect of the porous properties of the support, could bring deeper property-activity correlations than what was achieved by screening different supports and active metals. For the bimetallic catalysts, tuning the ratio between the noble metal and the base metal, and optimizing the preparation method with a target of improving the base metal dispersion, could be of interest.

Overall, this thesis brought new insights into the reaction network and impact of the catalyst composition on the activity and selectivity in the HDN and HDO of fatty amides and their derivatives.
Conclusions and outlook
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