Catalytic Hydrodeoxygenation of Lignin-Derived Oils

Towards the Production of Renewable Liquid Fuels

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Catalytic Hydrodeoxygenation of Lignin-Derived Oils

Catalytic Hydrodeoxygenation of Lignin-Derived Oils

Towards the Production of Renewable Liquid Fuels

Tove Kristensen

LUND
UNIVERSITY

DOCTORAL DISSERTATION

Doctoral dissertation for the degree of Doctor of Philosophy (PhD) in Chemical Engineering at the Faculty of Engineering at Lund University to be publicly defended on the 12th of December at 09.00 in Lecture Hall KC:A, at the Centre for Chemistry and Chemical Engineering, Naturvetarvägen 14, Lund, Sweden.

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Abstract:

Lignin has emerged as a promising renewable substitute to fossil-based feedstocks for the production of liquid fuels. It aligns with global initiatives and directives for the transition towards sustainability. Advancing the industrial implementation of catalytic hydrodeoxygenation (HDO) for converting lignin-derived oils into liquid fuels is a key avenue for the transition. The development of suitable catalysts for this process is crucial to improve its economic viability. Catalyst deactivation is a major challenge for the viability of the process. The challenge is highly attributed to the bulky and reactive components in the lignin-derived oils, leading to blockage of the pores and active sites.

This thesis describes how the catalyst activity can be maintained for the HDO process of lignin-derived oils while meeting industrial requirements. The work focuses on applied catalysis, including both a model compound and lignin-derived oils, and deals with how a Ni–Mo/δ-Al_2O_3 catalyst can be tuned for improving its performance in the HDO process. The work presented in this thesis emphasizes providing strategies for overcoming deactivation problems and insights into how the catalyst characteristics can be modified. Two main research strategies were investigated: (1) the use of dopants for the pretreatment of the Al_2O_3, including the impregnation of La and Ce precursors and heat treatment, and (2) the use of promoters, including the impregnation of noble metals (Pd, Pt, or Ir) onto the Ni–Mo/Al_2O_3 catalyst.

By including the pretreatment step of the δ-Al_2O_3 prior to impregnating the active metals, the Ni–Mo/Al_2O_3 catalyst demonstrated improved performance in the HDO process. Among several investigations that explored both the effect of the amount and the order of the impregnation of the La and Ce precursors, it was demonstrated that the most advantageous results were achieved when 1 wt% of each metal was impregnated separately, followed by heat treatment at 1100 °C. This was interpreted from achieving longer processing times and indications of better decarbonization over this catalyst. The pore size and the strength of the active sites were proposed to be the affecting parameters for the observed results.

Impregnating 0.5 wt% Pt onto the Ni–Mo catalyst supported on pretreated Al_2O_3 (simultaneously impregnated with 1 wt% of each La and Ce) was found to be promising for enhancing catalyst performance in the HDO process. Although the full potential could not be completely established, the proposed advantages of using the Pt-promoted catalyst for the HDO process were inferred from indications of improved hydrogenation capability. A reduced risk of polymerization and, consequently, catalyst deactivation was suggested.

Keywords:
Heterogeneous catalysis, Hydrodeoxygenation, Lanthanoid metals, Lignin valorization, Liquid fuels, Ni–Mo/Al_2O_3 catalyst, Noble metals, Renewable resources.

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We need to get our heads into the game

Contents

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Populärvetenskaplig sammanfattning

’Katalytisk hydrering av ligninbaserade oljor’ - vad innebär ens detta? Vad handlar avhandlingen om, och varför är detta ett relevant forskningsområde? Vi tar det steg för steg.

Vi börjar med begreppet katalys. Föreställ dig att du behöver ta dig från en punkt A, på ena sidan bergstoppar, till en punkt B på andra sidan. Hade du gått över topparna, eller tagit en väg genom bergstoppsdalen? Ponera att du inte väljer väg baserat på utsiktsmöjligheter… Snarare, du väljer den väg som går snabbast och kräver minst energi. Detta är katalys. Punkt A är molekylerna som ska reagera, punkt B är produkterna. Bergstopparna är aktiveringsenergin, dvs den energibarriär man behöver komma över för att reaktionen ska ske. Katalysatorn sänker energin som krävs, och gör att reaktionen går snabbare. Katalysatorn är vägen genom dalen. Denna avhandling handlar om hur katalysatorn, vägen, ska utformas för att den ska hålla så länge som möjligt och ha en tillfredsställande prestanda medan den används.

Mer specifikt, avhandlingen beskriver hur en katalysator kan utformas så att den är lämplig att användas i en process, vars syfte är att förbättra kvalitén av en olja som är producerad från en restprodukt från skogsindustrin (lignin). Med hjälp av katalysatorn så ska kvalitén av denna ligninolja förbättras så att den kan användas som bränsle till exempelvis fartyg och flyg. Forskningsarbetet beskrivet i denna avhandling är genomfört med förhoppning att bidra till avancera möjliggörandet av en industriell tillämpning av denna process.

Relevansen för detta forskningsområde tillskrivs dagens behov av att drastiskt påskynda omställningen till ett hållbart samhälle. Det råder vetenskaplig konsensus att den pågående klimatkrisen är ett resultat av förbränning av fossila bränslen och de associerade utsläppen av koldioxid. Vi behöver utnyttja biomassa, baserad på rester eller biprodukter, för framställandet av bränslen för att kunna bryta denna negativa trend. Lignin framhålls som en lovande potentiell råvara för denna omställning.

Lignin är i huvudsak en restprodukt från skogsindustrin, där den produceras i stora volymer (främst i pappers- och massabruk). Lignin är den beståndsdel i träd (växter) som gör dem robusta samt att vatten kan transporteras från rötter till bladverk. Däremot har användning av lignin, historiskt sett, begränsats till förbränning och intern energitillförsel. Denna begränsning härrör från lignins komplicerade struktur. Lignin är ett stort nätverk av kolväten, med många reaktiva sidogrupper (innehållande syreatomer). Resultatet av denna struktur är att oljor som framställts från lignin inte är stabila, vilket försvårar lagring, samt att dess kvalité inte uppfyller de krav som finns på bränslen. Kvalitén måste förbättras, och detta genom att primärt ta bort syreatomerna i de reaktiva sidogrupperna.

Hydrering är en process som bland annat används i konventionella raffinaderier för att ta bort svavel och kväve från fossila oljor. Tillämpning av motsvarande process, men för att ta bort syre från ligninoljor anses lovande. Däremot, en betydande anledning till att hydrering av ligninoljor inte är industriellt tillämpad i dagens samhälle, är relaterad till katalysatorn som behövs för denna process.

Problematiken ligger i att prestandan för katalysatorn snabbt försämras i denna process, vilket innebär att den ofta behöver bytas. Detta resulterar i att värdet för att göra denna industriella omställning, till att använda ligninoljor som råvara för produktion av bränslen, minskar. De stora reaktiva molekylerna i ligninoljorna, tenderar att fastna på katalysatorns yta (vägen). I sin tur kan inte andra molekyler ta sig fram och reagera, varpå prestandan går förlorad. Se det som att bergsgetter ställer sig framför vägen genom dalen.

Denna avhandling bemöter denna problematik, och beskriver hur en katalysator kan utformas för att bättre möjliggöra att dessa stora molekyler kan ta sig till och från ytan, och samtidigt vara bra för ändamålet (förbättra kvalitén på oljan). Resultaten som presenteras i detta arbete ger framförallt en inblick i hur tillverkningen av katalysatorn påverkar ytan och hur valet av material kan varieras för att förbättra dess prestanda. Den slutliga katalysatorn som presenteras inom detta arbete anses ha potential för att påskynda den industriella omställningen av att använda lignin som råvara för att producera bränslen.

List of included papers

I. **Kristensen, T.**, Hulteberg, C., Blomberg, S., Tunå, P., and Abdelaziz, O. (2023) Parametric Analysis and Optimization of Vanillin Hydrodeoxygenation Over a Sulfided Ni–Mo/δ-Al_2O_3 Catalyst Under Continuous-Flow Conditions, *Topics in Catalysis*, 66, 1341–1352, DOI: 10.1007/s11244-022-01762-8.

II. **Kristensen, T.**, Hulteberg, C., Wallenberg, R., Abdelaziz, O., and Blomberg, S. (2024) Promoting Effect of Ce and La on Ni–Mo/δ-Al_2O_3 Catalysts in the Hydrodeoxygenation of Vanillin, *Energy & Fuels*, 38, 9827–9835, DOI: 10.1021/acs.energyfuels.4c00898.

III. **Kristensen, T.**, Selimi, J., Elmroth Nordlander, J., Abdelaziz, O., Hulteberg, C., and Blomberg, S., Improving Hydrodeoxygenation Over Ni–Mo/Al_2O_3 by Tuning the Textural Properties of the Support via Doping with Lanthanoid Group Metals, *Manuscript Submitted.*

IV. **Kristensen, T.**, Margellou, A., Hallböök, F., Abdelaziz, O., Blomberg, S., Hulteberg, C., and Triantafyllidis, K. (2025) Effect of Noble Metals on the Performance of Ni–Mo Catalysts for the Hydrodeoxygenation of Lignin Oils to Fuels, *Sustainable Energy & Fuels*, 9, 6260–6268 DOI: 10.1039/d5se01014d.

V. **Kristensen, T.**, Jawerth, M., Sjö, H., Gustafson, J., Tunå, P., Dahlstrand, C., and Hulteberg, C., Improved Process Stability in Hydrodeoxygenation of Lignin-Derived Oils Using Graded NiMo/Al_2O_3 Catalysts Modified with La and Ce, *Manuscript Submitted.*

Author contributions

I. I contributed to the conceptualization and construction of the continuous-flow reactor system. I planned, synthesized the catalyst, and performed the study. I participated in the statistical data optimization and evaluated the rest of the results. I wrote the manuscript, with input from the other authors.

II. I contributed to the design and planning of the study. I synthesized the catalysts and performed the characterizations and the experiments. I evaluated the results with contributions from the other authors. I wrote the manuscript, with input from the other authors. I handled the submission.

III. I conceptualized and designed the study. I synthesized all samples, performed the characterizations, and participated in the experiments. I participated in the statistical data optimization and evaluated the rest of the results. I wrote the manuscript, with input from the other authors. I handled the submission.

IV. I participated in the design and planning of the study. I synthesized the catalysts. I participated in the experiments and the characterization. I participated in the evaluation of the data. I wrote the manuscript, with input from the other authors. I handled the submission.

V. I participated in the conceptualization, design, and planning of the study. I synthesized the catalysts and performed the characterization. I wrote the manuscript together with the other authors.

Other related papers

i. Hu, T., Gericke, S., Tong, X., Nykypanchuk, D., **Kristensen, T.**, Hulteberg, C., Stacchiola, D., Blomberg, S., Head, A. (2023) Interaction of Anisole on Alumina-Supported Ni and Mo Oxide Hydrodeoxygenation Catalysts, *The Journal of Physical Chemistry C*, 127, 19440–19450, DOI: 10.1021/acs.jpcc.3c02780

ii. Abdelaziz, O., Capanema, E., Ajao, O., **Kristensen, T.**, Hosseinaei, O., Benali, M., Hulteberg, C. (2023) A Rapid and Tunable Approach for the Fractionation of Technical Kraft Lignin, *Chemical Engineering Transactions*, 99, 67–72, DOI: 10.3303/CET2399012

iii. Selimi, J., **Kristensen, T.**, Qureshi, Z., Hulteberg, C., Abdelaziz, O., Catalytic Hydrodeoxygenation of Black Soldier Fly Larval Lipids and Co-processing with Vacuum Gas Oil into Biofuel Intermediates, *Manuscript Submitted.*

iv. Selimi, J., Jawerth, M., Abdelaziz, O., **Kristensen, T.**, Samec, J., Dahlstrand, C., Hulteberg, C., A 600-Hour Continuous Hydroprocessing of Kraft Lignin Enabled by a Graded Catalyst-Bed System, *Manuscript Submitted.*

Related conference presentations

Kristensen, T., Abdelaziz, O., Blomberg, S., Hulteberg, C. (2022) Parametric Analysis and Optimization of Vanillin Hydrodeoxygenation over a Sulfided Ni–Mo/δ-Al_2O_3 Catalyst under Continuous-Flow Conditions, *19th Nordic Symposium on Catalysis*, Poster presentation, Espoo, Finland.

Kristensen, T., Hulteberg, C., Wallenberg, R., Abdelaziz, O., Blomberg, S. (2023) Promoting Effect of Ce and La on Ni–Mo/δ-Al_2O_3 Catalysts in the Hydrodeoxygenation of Vanillin, *15th European Congress on Catalysis*, Poster presentation, Prague, Czech Republic.

Kristensen, T., Hulteberg, C., Hallböök, F., Elmroth Nordlander, J., Selimi, J., Abdelaziz, O., Blomberg, S. (2024) Tuning Performance of Ni–Mo Catalysts for the HDO of Lignin Oils to Fuels, *20th Nordic Symposium on Catalysis*, Oral presentation, Stavanger, Norway.

Kristensen, T., Hulteberg, C., Abdelaziz, O., Hallböök, F., Elmroth Nordlander, J., Corrêa de Araujo, A., Funke, A., Margellou, A., Triantafyllidis, K., Blomberg, S. (2024) Tuning performance of Ni–Mo catalysts for the HDO of lignin oils to fuels, *18th International Congress on Catalysis*, Oral presentation, Lyon, France.

Kristensen, T., Blomberg, S., Jawerth, M., Dahlstrand, C., Hulteberg, C. (2025) Tuning Performance of Ni–Mo Catalysts for the Hydrodeoxygenation of Lignin Oils to Fuels, *The 29th North American Catalysis Society Meeting*, Oral presentation, Atlanta, U.S.

Preface

I would like to express my gratitude and acknowledge the opportunity given by Christian Hulteberg, who offered me the role of an industrial PhD student while working at the company called Hulteberg Chemistry & Engineering AB in 2021. On the company's behalf, Christian secured funding and acceptance for participating in the three-year project '*FLEXI-GREEN FUELS*' (grant agreement no. 101007130), declared within the EU's Horizon 2020 programme beginning in 2021. Once again, in 2023, the company received funding from the Swedish Energy Agency to participate in the three-year project '*ECO-FORCE FUELS*' (project no. P2022-00537). Not only was the budget secured, allowing me to complete the doctoral education programme, but also to do so within projects that both intended to investigate the catalytic hydrodeoxygenation of lignin-derived oils to fuels. Additionally, Christian arranged all the administrative paperwork and the collaboration with Lund University.

Christian, thank you.

I would also like to express not only the implications but also the opportunities of conducting my research project in collaboration with the industry and within the objectives set by the funding projects. Since the funding was secured on behalf of the company, aligned with industry needs, and connected to the overall project goals of implementing large-scale biorefineries, the research project had to be framed accordingly. Furthermore, the explicit requirement to include commercial catalysts in the testing formed the foundation and starting point of my research project. While this imposed certain initial limitations on the project's scope, it also provided me with the fantastic opportunity to conduct research on a detailed level, with the possibility of having the results directly applied in the industry.

It has been a fascinating journey. And I'm grateful for it.

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It feels a bit ironic when you write about catalysis, and the grand writing process is nothing like it. The energy barrier to get the process started was high, and the rate of writing was slow. Instead, this thesis was purely coffee-fueled and sheer stubbornness-based. If one thing, the process was internally limited. But I was not consumed during the process. For this, I can only thank my support (blink).

My supervisors – without your guidance, there would have been more severe unwanted side reactions. Dr. Sara Blomberg, my main supervisor, thank you for your encouragement and generosity in always helping out, and your unconditional willingness to include me in your network. I never thought I would work at a synchrotrone and sing 'it was a happy dog'. You made my uncoordinated ideas structured, so to speak. Dr. Omar Abdelaziz, my co-supervisor, thank you for your immediate and endless refined feedback. If anything, it was always optimized for the set conditions. To both Dr. Per Tunå and Prof. Ola Wallberg, who were also my co-supervisors, thank you for balancing my stress activation level.

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My friends – you are the species that always balance the interactions, which a catalyst can never work without. Thank you for making the conditions favorable in every way. Everyone in my soccer team, Las Presidentas BK, without your stimulating effects, yet sometimes chaotic with chain reactions, you gave me the energy to proceed to the goal.

My family, especially my mum, dad, and sis – you were (are) my true buffer system that dealt with my fluctuating motivation and stress levels. When I was a radical species, you were the perfect solution. Thanks for all the lunch boxes. Yes, I should always listen to you. Now, and always, you are the best.

Without you all, this work would never have reached completion. Thank you.

Abbreviations

ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
DMDS	Dimethyl disulfide
EDX	Energy-dispersive X-ray
FTIR	Fourier transform infrared
GC	Gas chromatography
HDO	Hydrodeoxygenation
IUPAC	International Union of Pure and Applied Chemistry
MS	Mass spectrometry
RSM	Response surface methodology
SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TPD	Temperature-programmed desorption
TPR	Temperature-programmed reduction
WHSV	Weight hourly space velocity
XRD	X-ray diffraction

1 Introduction

This thesis is composed of an introductory framework essay and five appended papers. The introductory essay is intended to provide an understanding of the significance of the work, the research approach, and the overall aims. Key findings and knowledge development are also addressed and discussed. The five papers, included at the end, present the details of the scientific research findings. This chapter offers a descriptive background on the project's significance, the research scope (approach and research questions), and details of the outline of the thesis.

1.1 Transitioning to sustainable liquid fuel production

The advancement of liquid biofuel production from next-generation resources is essential. Taking action to enable this transition is crucial from both an environmental and a sustainable perspective. This aligns with global initiatives undertaken by researchers and policymakers to address the challenges that the world is facing [1]. Overall, reducing greenhouse gas emissions is a critical goal for achieving global sustainability. It is stressed that the use of petroleum-based fuels needs to be urgently minimized. One established approach to turn this negative trend is the use of renewable resources for fuel production [2–5].

However, the renewable resources currently used for liquid biofuel production (bioethanol, biodiesel, and renewable biodiesel) are primarily first-generation feedstocks, and concerns regarding their use are declared [6]. First-generation feedstocks include starch- or sugar-based resources and vegetable oils, which leads to competition with food production and, consequently, other global goals are overlooked (e.g., Sustainable Development Goals number 2: zero hunger) [7]. Their application is also limited because they are not as economically attractive as traditional petroleum-based fuel production [6]. Therefore, transitioning to next-generation feedstocks (e.g., waste, residues, and byproducts), which offer improved cost-efficiency, is considered highly important for achieving improved exploitation of liquid biofuels and greater sustainability [5].

1.2 Lignin as a feedstock for liquid fuels

Lignin is a renewable resource with the potential to play a significant role in the transition to next-generation liquid fuels, for example, in aviation and bunkers. Alongside cellulose and hemicellulose, lignin is one of the most essential components of lignocellulosic biomass, making it one of the most naturally abundant resources worldwide [8, 9]. It is considered a second-generation feedstock because it is primarily produced as a by-product in the forest industry, predominantly through the kraft pulping process at pulp and paper mills [10]. Globally, approximately 50–70 million tonnes per year of lignin are produced as a by-product, accounted as extensive available resource, at pulp and paper mills [11, 12]. Thus, lignin is accessible in substantial quantities and is regarded as an inexpensive resource [5]. However, the main drawback of using lignin as a feedstock is its structural complexity [13]. The identified advantages and disadvantages of utilizing lignin are summarized in Figure 1.1.

Lignin has a highly complex structure; it is an irregular, polyaromatic, three-dimensional web that provides structural rigidity and enables water and nutrient transport in plants [8, 9]. Its structure also varies depending on several factors, e.g., plant source and how it has been processed [14, 15]. Historically, its value as a renewable resource has therefore been limited, restricting its applications mainly to on-site energy recovery [9, 16].

Today, lignin is recognized as a promising resource just because of its aromaticity and high hydrocarbon content [5, 13]. Advancements in lignin valorization have become an attractive strategy to improve global sustainability and the bioeconomy of biorefineries [2, 16]. Currently, several technologies for converting lignin to oils are being developed (e.g., pyrolysis and hydrothermal liquefaction). However, due to the resulting properties of the lignin-derived oils, barriers to their direct use remain and need to be addressed.

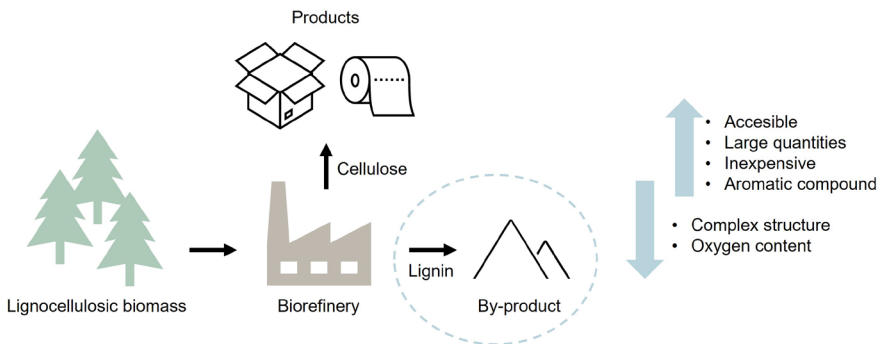

Figure 1.1. Illustration of lignin production, highlighting the identified advantages and disadvantages of utilizing lignin as a feedstock for renewable liquid fuels.

1.3 Upgrading of lignin-derived oils to liquid fuels

Upgrading of lignin-derived oils is required before they can be used as valuable fuels. Lignin-derived oils consist of large aromatic compounds that contain numerous reactive oxygenated functional groups, e.g., hydroxyl, methoxy, and carbonyl groups [17, 18]. Examples of oxygenated aromatic groups commonly found in lignin-derived oils are presented in Figure 1.2. As a result, their quality as a fuel is insufficient (e.g., low heating value attributed to high O/H ratio), and the oil's properties are both corrosive and unstable (causing, e.g., storage difficulties) [15, 18].

Currently, several initiatives are exploring opportunities to stabilize and enhance the quality of lignin-derived oils. Regardless of the approach, removing oxygen from lignin-derived oils is a necessary upgrading step. Among various techniques, catalytic hydrodeoxygenation (HDO) is considered one of the most promising methods for the removal of oxygen from lignin-derived oils [19, 20]. The HDO process, adapted from conventional refining processes (e.g., hydrodesulfurization) used for fossil-derived oils, offers several advantages (described in Chapter 2) for industrial application [5, 19].

For the HDO process, numerous different catalysts have been demonstrated to be active. Several valuable reviews have presented active catalysts for HDO, both those based on noble (e.g., Ru and Pt) and non-noble metals (e.g., Co, Fe, Ni, and Mo), supported on various materials, including oxides (e.g., Al_2O_3, ZrO_2, and TiO_2), zeolites (e.g., zeolite Socony Mobil-5 and ultra-stable Y zeolite), and carbon-based supports [3, 13, 19, 21]. However, given that lignin is predominantly derived from the kraft pulping process (which is associated with sulfur contamination in the resulting feedstock), the Ni–Mo/Al_2O_3 catalyst is considered particularly well-suited for adaptation in the HDO process and is commonly recognized for this application. This, among other reasons that will be discussed more in Chapter 2, was the foundation of using the Ni–Mo/Al_2O_3 catalyst as the starting point for this research project.

However, independent of the catalyst, deactivation is explicitly identified as a crucial challenge for industrial feasibility [5, 7, 13]. The development of a catalyst with prolonged activity in the HDO process is stressed as a key factor for advancing the use of lignin as a renewable resource in next-generation liquid biofuels [3, 20].

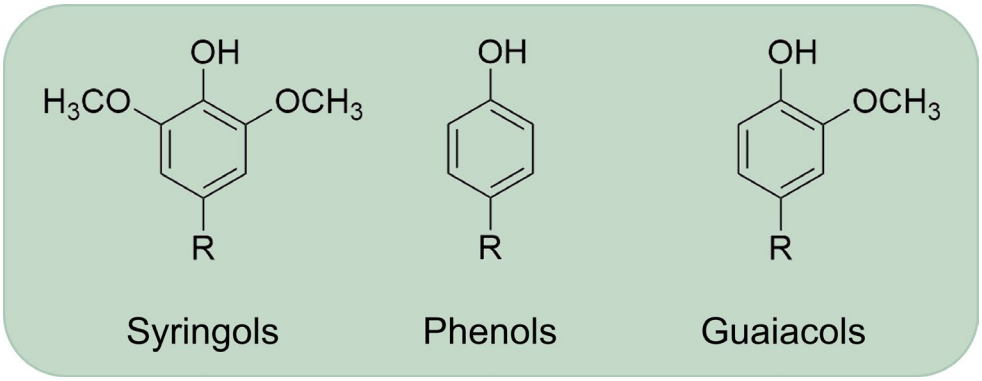

Figure 1.2. Examples of compounds in lignin-derived oils [18, 22].

1.4 Approach and research questions

This research project addressed the challenge of developing a catalyst suitable for use in the HDO process for upgrading the quality of lignin-derived oils to fuels. It was an interdisciplinary project, focusing on closing the gap between applied research and potential industrial application.

The overarching research objectives within this project were:

- To provide strategies for how challenges for the upgrading process of lignin-derived oils can be met while being compliant with industrial demands.
- To provide insights into how catalyst characteristics can be modified to enhance their performance in the HDO process.

With regard to enhancing the performance of the Ni–Mo/δ-Al_2O_3 catalyst in the HDO process, the objectives were addressed by investigating the formulated research questions (RQ):

RQ1: Is it advantageous to impregnate the support with La and Ce simultaneously, prior to heat treatment at 1100 °C? **(Paper II)**

RQ2: Is it advantageous to vary the amounts of La and Ce added to the support and the impregnation order of such, prior to heat treatment at 1100 °C? **(Paper III)**

RQ3: Is it advantageous to impregnate the doped Ni–Mo catalyst with a noble metal (Pd, Pt, or Ir)? **(Paper IV)**

RQ4: Is it advantageous to have a graded catalyst-packed bed in which the support pretreatment is the altering factor between the catalysts used in the top layer? **(Paper V)**

In this context, the term 'advantageous' referred to the aim of increasing HDO selectivity and achieving longer catalyst activity.

The investigation resulting in **Paper I** was conducted as a starting point, initiated with the intention of establishing a validated process system for further investigations. The aim was to construct a fixed-bed reactor system for performing the HDO experiments used to evaluate the performance of, initially, the Ni–Mo/δ-Al_2O_3 catalyst and essentially the modified catalysts investigated in **Papers II** and **III**.

1.5 Outline of the thesis

The thesis is composed of six chapters, representing the introductory framework essay, and five papers. Chapter 2 introduces the research area by providing an overview of the investigated process (the HDO process) and a description of the function of a catalyst, the risk for deactivation, and essentially the Ni–Mo/Al_2O_3 catalyst. The identified challenges and opportunities related to the research area are also described in Chapter 2. The strategies and the relevant methods used to address the core of this research project are described in Chapter 3. Key findings, knowledge development, and discussions are given in Chapter 4, whereas the conclusions from those are presented in Chapter 5. Finally, suggestions on future work are presented in Chapter 6.

2 Background

This chapter serves as a background to the research strategies, describing both the identified opportunities and challenges. To set the scene for the research and provide an understanding of the expectations of the catalyst, the chapter begins with an overview of the HDO process. The following sections outline the function of the catalyst and address concerns regarding deactivation. Lastly, a dedicated section presenting the Ni–Mo/Al_2O_3 catalyst is provided.

2.1 The hydrodeoxygenation process

The high oxygen content in lignin-derived oils restricts their further application. Upgrading, which includes the removal of oxygen, i.e., deoxygenation, from lignin-derived oils, is a necessary step to improve their suitability as liquid fuels [20, 21]. Commonly, deoxygenation is catalytically carried out under hydrotreatment conditions via the defined HDO reaction or via cracking reactions (i.e., decarbonylation and carboxylation), which remove oxygen as H_2O, CO, or CO_2, respectively [5, 23]. The preference for different deoxygenation reactions can vary depending on operational conditions and the catalyst employed, each with its own set of advantages and drawbacks. However, it is a complicated matter, and regardless of process design or the conditions set to favour a particular deoxygenation pathway, these reactions are known to occur in parallel [20].

Considering the identified advantages and disadvantages of the different deoxygenation processes, summarized in Table 2.1, the focus of this research project was to enable improved prerequisites for the HDO reaction (covered in **Papers I**–**V**). This focus was attributed to the current overall acceptance that HDO is a promising process for improving the industrial prospects for the utilization of lignin-derived oils as a liquid fuel [24]. The HDO process benefits from being adapted from traditional treatment processes used in conventional crude oil refineries, e.g., hydrodesulfurization. This is advantageous because existing infrastructure and hydrogen supply can be utilized. Additionally, a higher carbon content is preserved via the HDO reaction, resulting in better decarbonization, which aligns with regulatory targets.

Table 2.1.
An overview of different deoxygenation pathways and their main products, including hydrodeoxygenation and cracking (i.e., decarbonylation/decarboxylation). The associated relative advantages and disadvantages of each pathway are also summarized [5, 15, 19, 21].

Deoxygenation pathway	Product	Advantages	Disadvantages
Hydrodeoxygenation	H_2O	Implemented in the current refining infrastructure, improved decarbonization.	Requires hydrogen, high pressures.
Decarbonylation/ Decarboxylation	CO/ CO_2	No need for hydrogen.	Decreased preservation of carbon, high temperature, and expensive catalysts.

However, implementing the HDO process in refineries presents practical challenges. The thermal and chemical instability, as well as the corrosive properties of lignin-derived oil, can cause difficulties with storage and may damage process units. In addition, lignin-derived oils are known to be highly viscous and immiscible with other hydrocarbons [7, 13, 25]. Strategies have been developed to improve the feasibility of HDO implementation on a large scale. Common approaches include using a two-step process, which entails a primary mild stabilization step and a subsequent more severe HDO step, or co-processing lignin-derived oil with other hydrocarbon feedstocks prior to hydrotreatment [13, 26].

Within the framework of this research project, the experiments were designed to be relevant for the implementation of co-processed HDO, as reflected in **Paper V**. The underlying reason for applying co-processed HDO was based on the objectives set by the funding projects (as outlined in the Preface), which included the industrial implementation of the process in the near future. The different approaches were validated according to the current technical maturity of each process. Compared to two-step HDO, which is performed in standalone units, co-processed HDO takes advantage of existing refinery units. This approach requires lower capital investments and reduces the time to implementation [12, 27].

2.2 The function of a catalyst

Catalysis is a key tool in green chemistry and green engineering, both of which are essential for achieving sustainable development. A catalyst facilitates chemical reactions by changing the path to equilibrium by lowering the activation energy, without being consumed itself [28]. Thus, with an appropriate catalyst in a specific process, greater amounts of the desired product can be produced faster. Key concepts relevant to this research project, describing the performance of a catalyst, are presented in Figure 2.1.

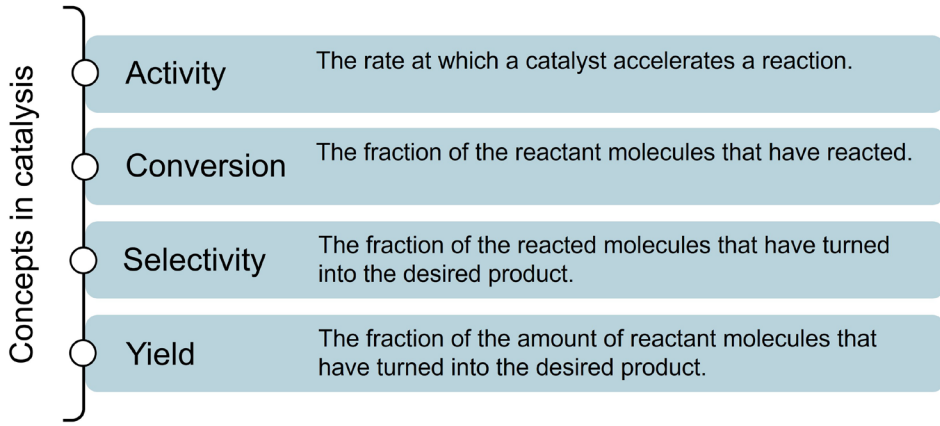

Figure 2.1. Key concepts relevant to the research project describing the performance of a catalyst [29].

However, depending on the process and practical or industrial needs, different subdisciplines of catalysis, e.g., heterogeneous and homogeneous catalysis, may be more or less suitable for application. In this research project, heterogeneous catalysis was employed. Heterogeneous catalysis implies that the catalyst and the reactant(s) are in different phases. This is the most applied subdiscipline in catalysis, accounting for approximately 90 vol% of the chemicals produced globally [30]. Additionally, the vast majority relies on solid catalysis. The main advantages of applying solid heterogeneous catalysis, relative to homogeneous catalysis, are the ease of separation between the catalyst and the products, its reusability, and thermal stability [26, 30].

Solid heterogeneous catalysis relies on surface reactions, which implies that surface interactions are key to its overall performance. As a result, heterogeneous catalysis is an interdisciplinary challenging subject, combining surface science with several other research areas (e.g., material science, physical and inorganic/organic chemistry, and process engineering). Consequently, tremendously many aspects of heterogeneous catalysis can be examined.

To simplify the complexity of describing heterogeneous catalysis, different principles are established within the community. Essential principles affecting the catalyst performance relate to active sites, the support, modifiers, and the synthesis of the catalyst [29]. These principles, which are described hereafter, are all crucial to consider when investigating and developing catalysts. An overview of a reactor and the catalyst bed, down to the support and the active sites, is presented in Figure 2.2.

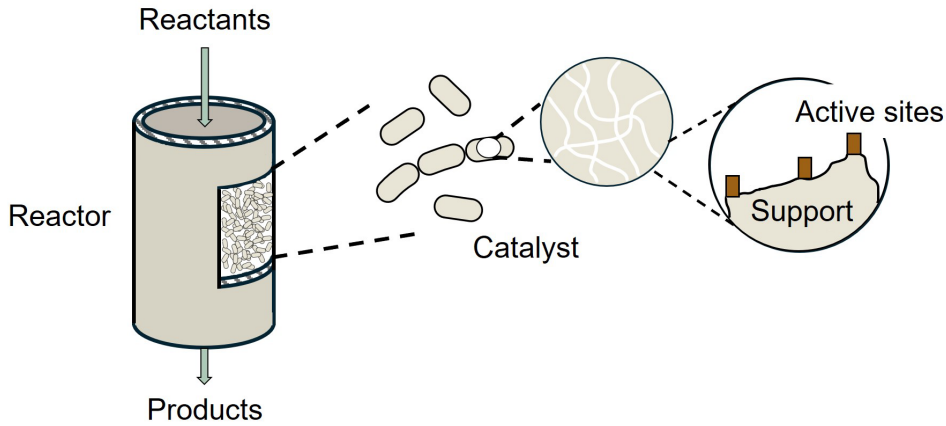

Figure 2.2. Illustration of the breakdown from a reactor and a catalyst bed down to the representation of the support and active sites.

- **Active sites**

For a reaction to occur, the reactants must diffuse to the surface, adsorb, and then react. The active sites are where these reactions take place. These sites are typically found at surface irregularities, where uncoordinated atoms provide options for interactions between the catalyst and the reactants [29]. The strength of these interactions at the active sites is also an essential factor for overall performance. The interactions must be strong enough for the reactants to adsorb but weak enough to enable the formation of intermediates, facilitate the reaction, and allow for the products to desorb (known as the Sabatier principle) [28]. Additionally, as described in more detail in Section 2.4.2, the nature of the active sites varies and should be considered in relation to the specific reaction they are intended to facilitate.

- **The support**

The support plays an essential role in the catalyst's overall performance. It provides mechanical and thermal stability. The use of a support also enables the possibility to increase the ratio of the amount of the active component, providing the active sites that are exposed for reactions (i.e., increase of dispersion) [29]. Higher dispersion generally leads to improved catalytic activity as more active sites become accessible. Importantly, the morphology of the support is in turn a decisive factor for the accessibility of these active sites. Supports are commonly porous materials, with active sites located within such cavities. Hence, the morphology of the support (e.g., shape and pore size) must be designed to allow reactants and products to diffuse to and from the active sites efficiently [29].

- **Modifiers**

Modifiers are components intentionally added during catalyst preparation, in small amounts, to improve the characteristics of the catalyst. Modifiers can be used to both enhance textural (e.g., surface area and pore size) and structural (e.g., atomic arrangement and interactions) properties of the support and/or catalyst [29]. Herein, modifiers are defined as dopants for components intentionally added during preparation to change textural properties, whereas promoters refer to components added to adjust structural properties.

- **Synthesis**

The synthesis of the catalysts, which includes all the steps of preparing the catalysts, is a complicated matter. Every decision made during synthesis influences the interactions among the components, and consequently, the characteristics of the catalyst. Not only do the choices of synthesis methods for the support and the active components (and the modifiers) affect the outcome, but also the choice of precursors, drying/calcination temperatures (temperature ramp and holding time) [31].

2.3 Catalyst deactivation

Naturally, given all the aspects that can affect catalyst performance, numerous unwanted effects can lead to a decrease in catalyst activity. Catalyst deactivation is a commonly encountered problem within catalysis. By understanding the causes of potential catalyst deactivation phenomena in a given process, more efficient catalysts can be designed to minimize such risks. Several general phenomena resulting in catalyst deactivation are recognized and are described in Figure 2.3. Deactivation phenomena specifically crucial for the HDO process are discussed in more detail in Chapter 3.

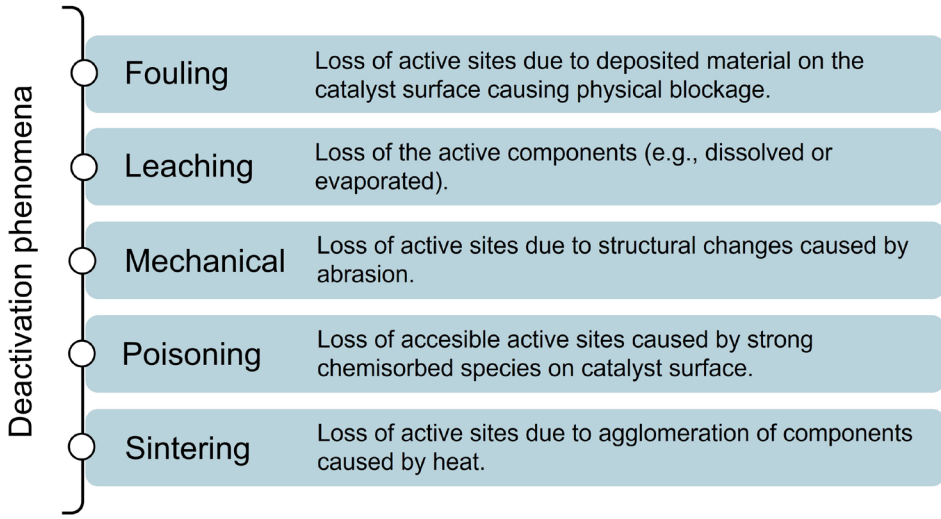

Figure 2.3. Overview of different catalyst deactivation phenomena [32, 33].

2.4 The Ni–Mo/Al_2O_3 catalyst

The Ni–Mo/δ-Al_2O_3 catalyst was selected as the primary catalyst used as the starting point for this research project. Given the objectives of the funding projects (implementing large-scale biorefineries as described in the Preface) and the associated framework established for this research project, the potential of using the Ni–Mo/δ-Al_2O_3 catalyst was considered to outweigh that of alternative catalysts. The reasons leading to the decision to adopt the industrial applied Ni–Mo/Al_2O_3 catalyst are presented in Section 2.4.1, while the HDO process using this catalyst is described in Section 2.4.2.

2.4.1 Prospects of the Ni–Mo/Al_2O_3 catalyst in the HDO process

Both the advantages and disadvantages of using the Ni–Mo/Al_2O_3 catalyst were identified and evaluated before deciding to adopt this catalyst as the starting point for this research project, as summarized in Figure 2.4. The profound reasons for selecting the Ni–Mo/Al_2O_3 catalyst were essentially for its advantageous attributes of being active for the HDO process and its compatibility with sulfur-containing feedstocks (i.e., lignin-derived from the kraft pulping process).

Certainly, the Ni–Mo/Al_2O_3 catalyst is also recognized as potentially problematic for use in the HDO process. In contrast to its advantage of being sulfur-tolerant, the Ni–Mo/Al_2O_3 catalyst actually requires sulfur to perform most efficiently [34, 35].

This dual dependency of sulfur often causes a debate regarding the relevance of conducting research on the Ni–Mo/Al_2O_3 catalyst for HDO of lignin-derived oils. A common argument against its relevance concerns the growing interest in lignin valorization. Intensified efforts are made to develop more environmentally friendly lignin separation processes, e.g., the organosolv process [17]. Unlike the currently predominant technique (at the time of the research project), the kraft pulping process, these techniques are developed to avoid the use of sulfur components. Given the expectation that these emerging separation techniques will become more prevalent in the future, it is argued that the Ni–Mo/Al_2O_3 catalyst may not remain relevant for the HDO of lignin-derived oils.

However, to enable the gradual adoption of the HDO process at refineries, it is necessary to conduct parallel research and development of different catalysts for this purpose. Thus, despite the argument that the Ni–Mo/Al_2O_3 catalyst may not be relevant for the HDO process of lignin-derived oils in the future, due to its sulfur dependency, this catalyst was still considered appropriate for this research project. The research project aims to enable industrial implementation of processes that convert lignin-derived oils to liquid fuels in the near future. This implies treating lignin-derived oils processed from kraft lignin. Kraft lignin can contain up to about 3–7 wt% sulfur [36]. Depending on the depolymerization technique and how the lignin is processed, varying amounts of sulfur end up in the resulting lignin-derived oils. Only trace amounts of sulfur (at ppm levels) are known to poison, for example, noble metal-based catalysts and subsequently lead to their deactivation [18, 21]. Although other sulfur-tolerant catalysts, e.g., CoMo/Al_2O_3 and CoW/Al_2O_3, were considered, they were ultimately not selected due to practical and safety reasons.

Another argument in favour of adopting the Ni–Mo/Al_2O_3 catalyst for this research project is its current use in conventional refineries. The Ni–Mo/Al_2O_3 catalyst is already applied in conventional hydrotreatment processes for fossil-derived oils, just because of its activity in removing heteroatoms (i.e., sulfur and nitrogen) [21]. As discussed in Section 2.1, HDO strategies have been developed to facilitate the gradual adoption of lignin-derived oils as a feedstock for liquid fuels. Considering the favourable approach of co-processing lignin-derived oils with hydrocarbons prior to hydrotreatment at conventional refineries, the Ni–Mo/Al_2O_3 catalyst was validated as even more suitable compared to other catalysts.

Additionally, the successful use of the Ni–Mo/Al_2O_3 catalyst in the refining industry for fossil-derived oils can also be attributed to its mechanical strength and low cost, both of which are attractive prerequisites for industrial application. This was also validated in favour of its use compared to other potential catalysts, e.g., noble metal-based, which are relatively more expensive [26].

Aside from the described drawback of sulfur dependency, the use of the Ni–Mo/Al_2O_3 catalyst is also recognized to be problematic due to other aspects. It is known to be sensitive to H_2O exposure (primary product in HDO) and to possess

strong acidic properties [34, 37–39]. Nevertheless, compared to sulfur dependency, H_2O sensitivity and acidity were considered secondary and less significant drawbacks during the evaluation of different catalysts for this research project. In fact, these challenges were addressed in the assessment of various strategies aimed at improving the prospects of the Ni–Mo/δ-Al_2O_3 catalyst, as discussed more in depth in Chapter 3.

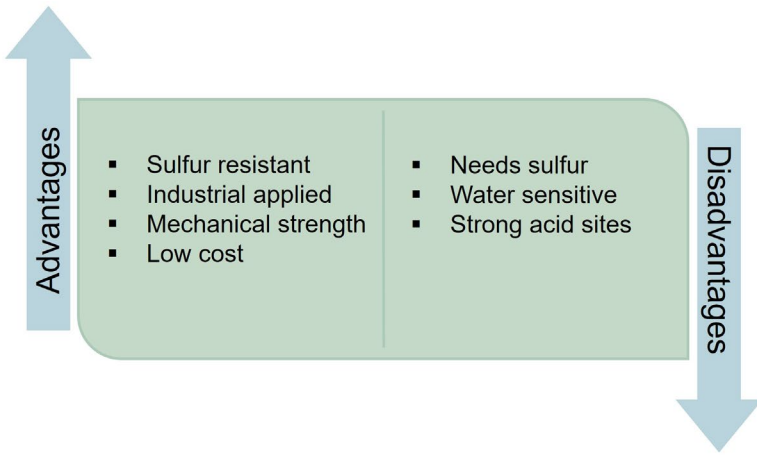

Figure 2.4. A summary of the advantages and disadvantages of using the Ni–Mo/Al_2O_3 catalyst in the HDO process of lignin-derived oils.

2.4.2 HDO over the Ni–Mo/Al_2O_3 catalyst

In Section 2.2, concepts in catalysis were presented. The importance of understanding the function of the active sites and the support for enabling the possibility of affecting the performance of the catalyst was described. In this section, those aspects are discussed in relation to the Ni–Mo/Al_2O_3 catalyst. The functions of the various components in this catalyst are described from the perspective of their role in the HDO process.

The first aspect of the catalytic HDO mechanism is for the reactants, the oxygenated compounds, to adsorb onto the active sites. For the sulfided Ni–Mo/Al_2O_3 catalyst, the main active sites are usually considered to be so-called coordinatively unsaturated sites. These consist of S vacancies in the MoS_2 structure, resulting in Mo sites with a sub-stoichiometric number of neighbouring S atoms [34, 40]. The size of these MoS_2 layered structures (i.e., also-called 'sandwich structure') is affected by metal interactions and preparation methods. The edges of the MoS_2 structures are recognized as being the most catalytically active. The Ni species promotes the formation of the unsaturated sites, resulting in enhanced activity [40, 41].

The unsaturated sites are known to be Lewis acidic. Lewis acid sites accept electron pairs, meaning that these sites interact with the oxygenated compounds, resulting in the adsorption of such. The compounds form intermediates on the surface, which, together with the supply of hydrogen, result in deoxygenation [21]. An illustration of the HDO mechanism is described in Figure 2.5.

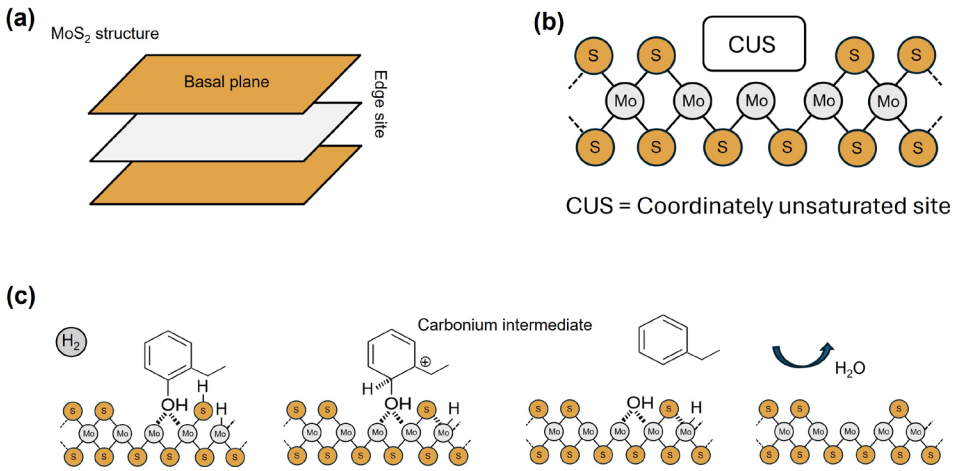

Figure 2.5. Illustration of (a) the MoS_2 structure, (b) the coordinately unsaturated sites, and (c) the HDO process of 2-ethylphenol, the mechanism proposed by Romero et al. and adapted [42].

For the Ni–Mo catalyst, porous transition Al_2O_3 (the meaning of this will be discussed more in Chapter 3) is recognized for being a beneficial support for this process. The porous transition Al_2O_3 provides high mechanical strength and a high surface area, with acidity allowing for sufficient interactions with the active metals, providing good dispersion of such.

3 Catalyst formulations – strategies, synthesis, and characterization techniques

In the previous chapter, the background to the research area was described, covering aspects related to the HDO process, catalysis, and the Ni–Mo/Al_2O_3 catalyst. This chapter presents the core of the research project. The strategies identified for modifying the characteristics of the Ni–Mo/δ-Al_2O_3 catalyst, aimed at reducing the most evident risk of deactivation during the HDO process, are described. The context and rationale behind the formulated research questions are explained. Following this, the applied catalyst synthesis method is outlined. Finally, the characterization techniques used to provide insights into how modification strategies have affected the properties of the synthesized catalysts are described.

3.1 Modification strategies

As described in Chapter 2, several phenomena can lead to catalyst deactivation, including fouling, leaching, mechanical, poisoning, and sintering (Figure 2.3). Certainly, all of these deactivation phenomena may occur during the HDO process of lignin-derived oils. The literature contains several relevant studies highlighting research related to these deactivation phenomena in this process [40, 43, 44]. However, the most evident cause of catalyst deactivation in the HDO process of lignin-derived oils is carbon deposition on the catalyst surface (i.e., fouling) [45].

Not only can carbon deposit on the catalyst surface lead to deteriorated catalytic performance, but it can also lead to pressure drop and disruption of the process. The carbon deposition formed on the catalyst surface results from diffusion limitations due the the large, bulky phenolics in the lignin-derived oils and as a consequence of their affinity for polymerization [46, 47]. Consequently, this leads to blockage of pores and active sites, and ultimately, catalyst deactivation.

Therefore, the strategies addressed in this research project were aimed at improving diffusion and reducing the risk of polymerization. The identified strategies involved modifying the support and the catalyst with dopants and promoters (as defined in

Section 2.2), respectively. These strategies and their rationale are described in greater detail in Sections 3.1.1 and 3.1.2.

3.1.1 The use of dopants

To allow for improved diffusion, the textural properties of the catalyst need to be shaped appropriately. In this context, increasing the pore diameter was considered desirable. The pore diameter should be several times larger than the molecule size to allow for less diffusion restriction [48, 49]. Therefore, while evaluating the potential of using the Ni–Mo/δ-Al_2O_3 as the primary catalyst used as the starting point for this research project, possibilities for enhancing its textural properties were also explored. The Ni–Mo/δ-Al_2O_3 catalyst was regarded as promising in this aspect. The possibility of improving its textural properties is attributed to the ability to modify the texture of the support.

The original support (δ-Al_2O_3) belongs to the category of porous transition Al_2O_3. Transition Al_2O_3 is a complex material whose texture depends on its manufacturing method. Generally, the bulk material of transition-Al_2O_3 consists of ordered crystalline grains and disordered amorphous phases, which together form a mesoporous structure with intraparticle voids. These grains are polymorphs, meaning that several crystalline phases can coexist [50]. Additionally, the crystalline phases present in the transition-Al_2O_3 are not thermally stable. Upon heat treatment, the metastable crystallites (from γ-, δ-, and θ-phases) can transform into the thermally stable α-phase [51]. This transformation is also associated with pore enlargement, which is in line with the desired outcome of the strategy outlined here [52]. Thus, the primary speculation of how to intentionally increase the pore diameter of the Ni–Mo/δ-Al_2O_3 catalyst involved a pretreatment step in which the δ-Al_2O_3 was exposed to 1100 °C prior to the subsequent synthesis steps (as explained in Section 3.2). The temperature of 1100 °C was selected following an in-house investigation that evaluated the temperature required to achieve an increase in pore diameter.

In association with the heat treatment of the δ-Al_2O_3, and as part of evaluating this modification strategy, it was primarily speculated that the heat treatment also would be beneficial to meet other concerns raised about using the Ni–Mo/δ-Al_2O_3 for HDO of lignin-derived oils. As discussed in Chapter 2, the possession of strong acid sites and sensitivity to H_2O are raised as drawbacks, and uncertainty about its suitability for the HDO process has been reported [13]. However, thermally more stable Al_2O_3 phases tend to exhibit a lower amount of strong acid sites. Thus, the proposed heat treatment was considered promising to lower the risks associated with strong acid sites (e.g, polymerization). Furthermore, the sensitivity to H_2O is believed to be due to, e.g., possible hydration of the metastable transition-Al_2O_3, leading to decreased promoting effect of Ni and, consequently, reduced catalytic activity [13, 38]. However, it is believed that the less stable transition-Al_2O_3 phases are the most

sensitive to H_2O. Thus, it was speculated that including the pretreatment step of the δ-Al_2O_3 could also help decrease its sensitivity to H_2O.

However, a recognized disadvantage of heat-treating transition-Al_2O_3 is that it also leads to sintering, which consequently results in the loss of surface area [52]. Thus, the area of the Al_2O_3 available for the distribution of the active metals is reduced, which could lead to fewer available active sites. In turn, lower activity is anticipated, which is not the desired outcome. For this reason, neither θ-Al_2O_3 nor α-Al_2O_3 was used directly as a support. The δ-Al_2O_3 was, however, believed to be more appropriate to be used as the initial support for the Ni–Mo catalyst instead of γ-Al_2O_3. The γ-Al_2O_3 is otherwise recognized as the most commonly used support for Ni–Mo catalysts employed in hydrotreatment processes. The δ-Al_2O_3 was considered to be more appropriate as it also contains fewer strong acidic sites compared to γ-Al_2O_3, which was also identified as a disadvantage for the application of this catalyst in the HDO. Nevertheless, in accordance with the research questions (RQ1, RQ2, and RQ4), La and Ce precursors, referred to as the dopants, were impregnated onto the δ-Al_2O_3 prior to its heat treatment. The main intention behind impregnating the δ-Al_2O_3 with La and Ce precursors was to preserve the surface area during the heat treatment. An overview of the primary purpose for using these dopants is illustrated in Figure 3.1.

The choice of impregnating the δ-Al_2O_3 with La and Ce precursors prior to the heat treatment was based on studies found in the literature [53–58]. These metals have attracted attention for their ability to provide thermal stabilization and improve catalyst characteristics. In particular, La is reported for its stabilization abilities, while Ce is for increasing the dispersion of the active metals. Both of these effects were considered relevant for this research project. However, at the time this research was conducted, most literature describing these advantages focused on other processes, such as partial oxidation and reforming. Fewer reports addressed the use of these dopants in catalysts for the HDO process, but their application was still encouraged [59–61].

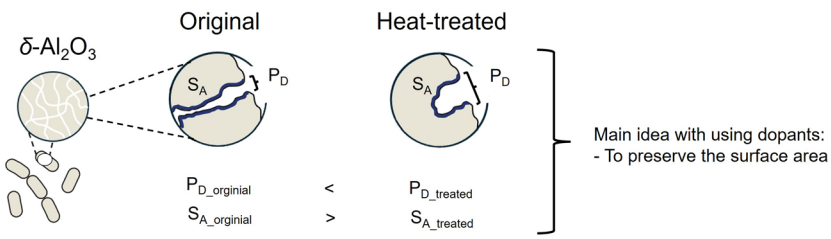

Figure 3.1. Illustration of the main idea behind using dopants to modify the support. SA and PD denote surface area and pore diameter, respectively.

3.1.2 The use of promoters

Enhancing the hydrogenation capability of the catalyst was identified as a promising strategy to reduce the risk of polymerization. During the deoxygenation reaction, unstable carbonium intermediates (electron-deficient carbon intermediates) are formed. These carbonium intermediates are prone to further reaction, including polymerization [49]. Thus, the primary objective in improving the hydrogenation capability of the Ni–Mo/δ-Al_2O_3 catalyst was to enable faster saturation of these carbonium intermediates with hydrogen, thereby decreasing the likelihood of polymerization. By introducing a promoter that facilitates hydrogen dissociation on the catalyst surface, less time in the carbonium intermediate state was anticipated, and consequently, resulting in lower amounts of carbon deposition on the surface [21].

Noble metal-based catalysts are recognized for their hydrogenation capability and are reported as promising for the HDO process [13, 15, 18]. Nevertheless, due to their high cost and sensitivity towards sulfur, the application of these catalysts was not initially considered appropriate in this research project. However, it was found that minor amounts of Pt had been demonstrated to improve the activity of a sulfided Co-Mo/Al_2O_3 catalyst used for hydrodesulfurization [62]. Additionally, improved sulfur tolerance for noble-based catalysts has been demonstrated for noble-based catalysts when varying the properties of the support [63, 64].

Considering the above aspects and the industrial demands for cost efficiency, the impregnation of 0.5 wt% of noble metals onto the Ni–Mo catalyst was evaluated as a potential strategy to improve the hydrogenation capability of the catalyst. As a consequence, improved HDO activity and longer processing times were anticipated. An overview of the main purpose of using the promoters is illustrated in Figure 3.2.

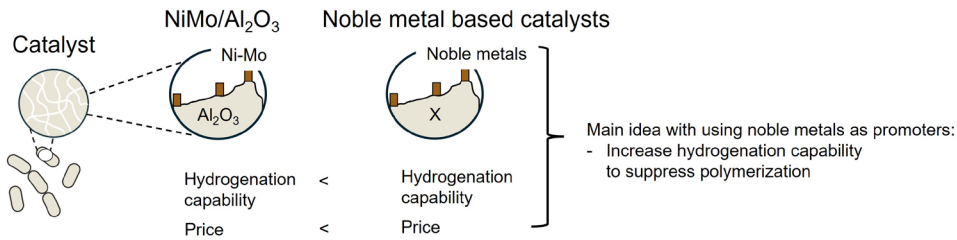

Figure 3.2. Illustration of the main idea behind using noble metals as promoters.

3.2 Synthesis method

The term “synthesis” refers to the entire process of preparing the catalysts. In this context, the synthesis includes two main steps: impregnation and heat treatment. Each step consists of procedures that were consistently employed throughout the

research project (to limit possible factors influencing catalyst characteristics), as well as procedures that were varied in accordance with the formulated research questions. This section provides an overview of the synthesis process. An illustration of the synthesis is presented in Figure 3.3.

- **Impregnation**

Impregnation, which involves introducing metals onto the solid surface, was consistently performed using the incipient wetness method [29]. This method is commonly used for synthesizing heterogeneous catalysts. It includes preparing a precise volume of metal precursor solutions, which are then used for the impregnation. This method allows for homogeneous impregnation and minimizes waste (compared to, for example, the wet impregnation method). The method includes:

1. Determination of the amount of the solution needed to saturate the pores of the solid material.
2. Weighing of the materials and preparation of solutions.
3. Impregnation.

H_2O was used to determine the pore volume of the solid material as well as to serve as the solvent. Throughout the project, the same support material (δ-Al_2O_3) and the same active metal precursors were employed. Keeping the amounts of active metals consistent enabled a more precise evaluation of the factors influencing catalyst performance in the HDO process and facilitated the investigation of the research questions. The variables adjusted and assessed during the impregnation step, in accordance with the research objectives, included the use of dopants (their quantities and order of impregnation, as described in **Papers II**, **III**, and **V**) and promoters (**Paper IV**).

- **Heat treatment**

The purpose of the heat treatment is to form the properties of the solid material in a controlled manner. The heat treatment step allows for the formation of bonds between the impregnated metal and the solid material, and involves two steps:

4. Drying
5. Calcination

Drying is conducted at a lower temperature to remove the solvent (H_2O) without causing a collapse of porous material. Subsequently, calcination is performed at higher temperatures to enable decomposition and evaporation of the metal-salt precursor, resulting in the formation of bonds between the metal and the solid material [29].

A temperature ramp of 2 °C/min was consistently applied to reach both the set drying temperature (120 °C) and the calcination temperature (500 °C) for the active components (Ni, Mo, and the noble metals, respectively). The calcination procedure involving the impregnation of dopants was, in accordance with its purpose and the research questions, carried out at higher temperatures (1100 °C or 1250 °C). A lower temperature ramp of 1 °C/min was used from 900 °C when preparing the catalyst used in investigations reported in **Papers III** and **V**.

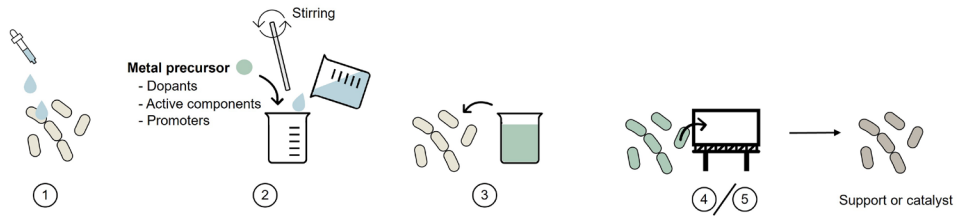

Figure 3.3. An overview of the synthesis steps: (1) H_2O uptake, (2) preparation of solutions, (3) impregnation, (4) drying, and (5) calcination.

3.3 Characterization techniques

Considering the numerous aspects influencing the properties of the prepared solid material (support and/or catalyst), as described in Section 2.2, isolating the true effects of the varying factors (e.g., addition of dopants and promoters) is challenging. To meet this challenge, the exploitation of several techniques is required to gain a sophisticated understanding of how the different factors affect the characteristics of a solid material. However, availability, time, and costs become factors to consider in relation to its purpose. The characterization techniques applied in this research project are described hereafter. The papers in which the different techniques have been employed for the investigations are also presented.

- **Physisorption** – *all papers*

With N_2 as the probing molecule, physisorption analysis was performed to gain knowledge of the textural properties (specific surface area, pore diameter, and volume) [65]. Understanding the textural properties provides a foundation for discussing accessibility of the active sites, which is of great importance for being able to discuss possible differences observed in the HDO process. This analysis is advantageous, as it is non-destructive and time-efficient for the amount of information it provides. Certainly, physisorption is a powerful tool for providing textural properties. However, the precision of the technique is limited to the mesopore range of 2-50 nm [66].

The technique involves the determination of the N_2 adsorption and desorption isotherms (at a temperature of liquid nitrogen, i.e., -196 °C). These isotherms are obtained via stepwise dosing of known amounts of N_2, from which the amount of adsorbed N_2 can be calculated based on the relative pressure (pressure of gas/saturation pressure of N_2 at -196 °C). Initial measurements, from vacuum up to atmospheric pressure, provide the adsorption isotherm, while the desorption isotherm is obtained as the measurements proceed from atmospheric back down to vacuum conditions. Using these isotherms, the surface area and pore size can then be determined using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methodologies, respectively [67, 68]. Additionally, the shape of the isotherms provides information about the pore structure. According to the various types of isotherms and hysteresis loops classified by the International Union of Pure and Applied Chemistry (IUPAC), insights regarding pore size distribution and pore shape can be obtained [65].

- **X-Ray Diffraction** – *Papers II–V*

The X-ray diffraction (XRD) technique was employed to obtain information about the crystallinity present in the support and catalysts, to identify any new crystalline phases formed as a result of dopant and active metal impregnation, and to evaluate crystallite sizes. However, diffraction patterns are only generated by crystalline structures larger than a few nanometres, which restricts the evaluation [28]. This means that the technique provides information related to the bulk rather than surface species.

The technique involves probing the sample with an X-ray beam (of known wavelength, dependent on the source). Depending on the interaction with the crystal planes, the X-rays are scattered differently. Using a connected detector, the intensity of the scattered X-rays can be measured, enabling the generation of a diffraction pattern [69]. This pattern works like a fingerprint and can be used to evaluate the crystalline phases present in the sample. Nevertheless, diffraction from several phases can overlap, and identification can be challenging. As an analytical and mathematical tool for obtaining quantitative information about the crystal structure, Rietveld refinement can be used [70].

- **Scanning Electron Microscopy –** *Papers I, II, and IV*

Scanning electron microscopy (SEM) was used to evaluate the morphology of the catalyst samples. The instrument was equipped for energy-dispersive X-ray (EDX) spectroscopy, which also allowed for the investigation of the elemental composition.

For this technique, an electron beam scans the sample, resulting in the ejection and backscattering of electrons. A connected detector measures the intensity of these secondary electrons and translates the data into an image [29]. Additionally, by

using an EDX detector, the emitted X-rays can also be detected, allowing for the collection of spatially resolved information about the elements present on the surface.

- **X-Ray Fluorescence** – *Paper II*

The X-ray fluorescence (XRF) technique was used as a complementary analysis to gain a better understanding of the elemental composition of the synthesized catalysts [69]. Compared to SEM-EDX analysis, XRF provides compositional information across a larger area, resulting in a more representative overview of the sample.

The principle of detection in XRF is similar to that of SEM-EDX, as both rely on X-ray photons with energies characteristic of specific elements [69]. However, instead of probing with electrons as in SEM, XRF uses X-rays to eject electrons from the atom's inner shells. An advantage of using XRF to evaluate elemental composition is that X-rays penetrate deeper into the sample, allowing for a more accurate estimation of metal loading.

- **Temperature-Programmed Reduction** – *Papers II, III, and IV*

Temperature-programmed reduction (TPR) was employed, using H_2 as the probing gas, to assess the reducibility of the catalysts and to provide insight into the interactions between the metals and the support [71].

In this technique, a mixture of hydrogen and an inert gas is flowed over the sample while heating. The outgoing gas passes through a TCD, which records the amount of hydrogen consumed. However, a challenge with TPR is that different species can reduce at similar temperatures, making it difficult to determine which consumption peak corresponds to which species.

- **Chemisorption** – *Papers II–V*

Static chemisorption, using NH_3 as the probe molecule, was performed to quantify the total amount of acid sites (both Lewis and Brønsted acid sites) on supports and catalysts, which is an important property that enables discussion about activity [72].

This measurement involves dosing known amounts of the probe molecule, stepwise, at a constant temperature. Equilibrium is allowed to be reached after each dose. The initial and the pressure at equilibrium are measured, from which the adsorbed amount can be calculated. During the primary adsorption measurement, both chemisorbed and physisorbed species are determined. Afterwards, the physisorbed molecules are removed by pumping, and a second measurement is performed. During the second measurement, the physisorbed amount can be measured. From these two measurements, the chemisorbed amount can be calculated. However, in the context of this research scope, a drawback of using NH_3 as the probing molecule

is its small size compared to lignin-derived molecules, which can lead to an overestimation of accessible sites.

For the investigation reported in **Paper IV**, chemisorbed pyridine was used to distinguish between the amount of Lewis and Brønsted sites by applying Fourier transform infrared (FTIR) spectroscopy.

- **Temperature-Programmed Desorption** – *Papers II, III, and V*

Temperature-programmed desorption (TPD), using NH_3 as the probing molecule, was performed to gain an understanding of the strength of the acid sites. The strength of the acid sites is also important to evaluate for the discussion of catalyst activity [28].

During TPD, the already probed sample (chemisorbed NH_3) is heated while flowing an inert carrier gas. By measuring the outgoing gas with a TCD, the amount of desorbed NH_3 within the set temperature range can be determined. This process allows for the assessment of acid site strength, as stronger interactions require higher temperatures for desorption.

4 Catalyst performance in the hydrodeoxygenation process

This chapter essentially presents the key findings together with discussions. Details are found in the corresponding embedded papers at the end. Nevertheless, insights are described, explaining how findings have been interpreted and used for decision-making when framing new investigations. The chapter begins with a section providing an overview of the workflow during the research project. The following sections present the investigations related to **Papers I**–**V**.

4.1 Workflow of the research

Research that combines a detailed understanding of catalyst characteristics with applied catalysis is particularly challenging. The interpretation of the results is especially complex when dealing with diverse feedstocks like lignin-derived oil.

Therefore, as a starting point, a model compound was used for the primary investigations (**Papers I**–**III**). The reason for using a model compound is primarily to simplify the interpretation of results. However, to more accurately determine the potential of the catalysts from an industrial perspective, it is also important to use real lignin-derived oil to gain an improved understanding. Therefore, key findings from the investigations presented in **Papers II** and **III** were subsequently applied to further research using real lignin-derived oils in work related to **Papers IV** and **V**, respectively.

Additionally, although the Ni–Mo/δ-Al_2O_3 catalyst was intentionally used because most lignin-derived oils are produced via the kraft process (which contains sulfur, as discussed in more detail in Chapter 2), investigations related to **Papers II** and **IV** also evaluated whether catalyst modifications affected the need to co-process sulfur to maintain activity. This approach aimed to provide a parallel understanding of the potential application of these catalysts for the upgrading of lignin-derived oils not processed from kraft lignin.

An overview of the workflow is illustrated in Figure 4.1. Figure 4.1 summarizes the investigations and presents the main purpose of the papers (correlated to the titles

used for Sections 4.2-4.5, which describe the work and key findings in **Papers I**–**V**, respectively), the feedstock and the catalysts used, and the order in which the papers have been established.

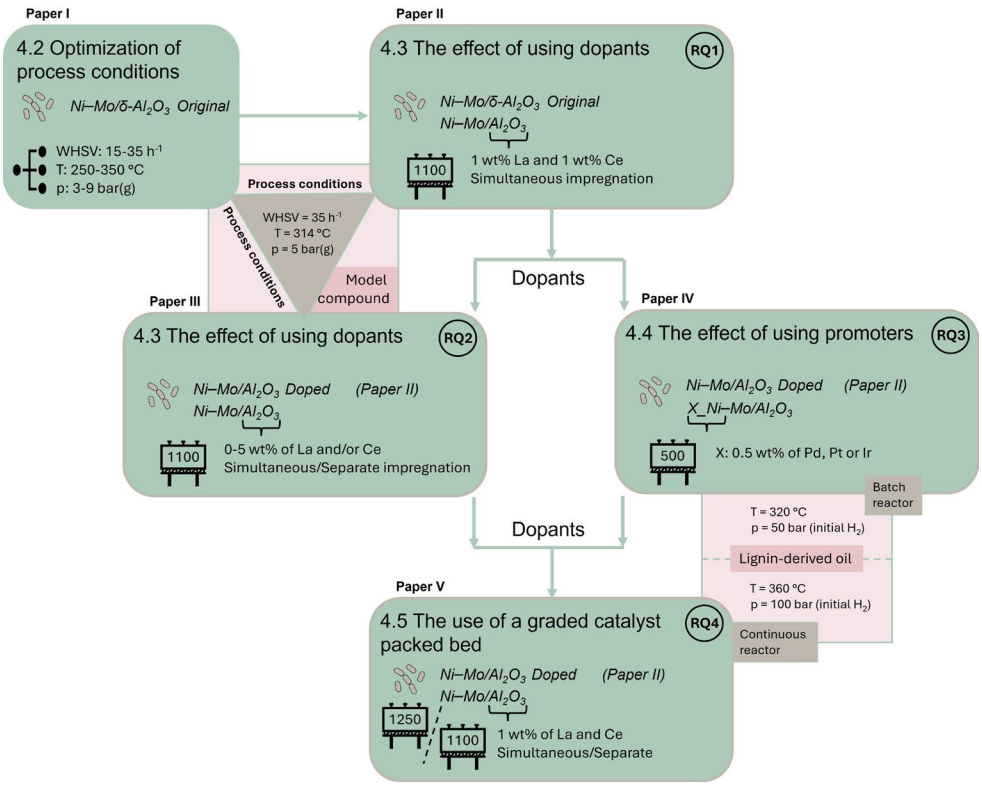

Figure 4.1. An overview of the investigations performed in the presented research thesis, including the section headings where key findings are presented and discussed.

4.2 Optimization of process conditions

Catalyst modifications affect the outcome, but the feedstock and the process conditions also synergistically influence the results. This means that for a given feedstock, different catalysts may require different process conditions to perform most beneficially. It is therefore challenging to determine if an intentional modification of the catalyst is advantageous for the process or not, and to decide how to proceed and what to consequently investigate [15].

Therefore, as an essential step in this research project, an investigation was conducted to understand the performance of the Ni–Mo/δ-Al_2O_3 catalyst (aimed to

be modified) for the HDO process. As described in Section 4.1, a lignin-model compound (vanillin) was used for the HDO experiments performed under continuous-flow conditions to simplify the interpretation of results. The aim of this investigation was also to establish a verified experimental setup for the HDO process intended for use in subsequent investigations. To establish a basis for evaluating the potential advantages of the modified catalysts, the optimal conditions for achieving the desired outcome using the Ni–Mo/δ-Al_2O_3 catalyst in its sulfide state were also determined.

The results from these investigations were reported in **Paper I**, which is summarized in this section. Evaluations done for making appropriate decisions related to framing the investigation are discussed in Section 4.2.1, while the findings are summarized in Section 4.2.2.

4.2.1 Design of the experiments

The feedstock

There are tremendously many papers published about HDO of lignin-model compounds in reputable journals focused on sustainability, lignin valorization, and fuels. Within the research community, there is a clear consensus that employing representative lignin-model compounds (a diversity of phenolic compounds) provides a relevant foundation for work in this field. However, aromatic compounds containing one or two functional groups (e.g., cresol or guaiacol) are most commonly used for HDO processes conducted under continuous-flow conditions.

To further investigate the process, vanillin, an aromatic compound with multiple oxygenated functional groups (aldehyde, hydroxyl, and ether), was selected as a representative lignin-model compound [73]. The instability of real oil is largely attributed to the reactive carbonyl groups [74]. However, since vanillin is solid at room temperature, a solvent was required to perform the experiments under continuous-flow conditions. After evaluating various options, xylene was chosen for its aromaticity, lack of oxygen, and its ability to dissolve reasonable amounts of vanillin. Other solvents, e.g., ethanol, have been reported in the literature, but concerns about vanillin precipitating during heating and potentially clogging the system have been raised [75]. The suitability of xylene as a solvent was tested prior to the investigation.

The reactor system

A substantial number of studies investigating the HDO of lignin-model compounds have been conducted using batch reactors [15]. However, to better understand the process as applied in industry, where continuous reactor systems are predominantly used, a continuous-flow fixed-bed reactor was chosen for this investigation. For this

purpose, an in-house experimental system was constructed. An illustrative diagram of the continuous-flow reactor system is shown in Figure 4.2.

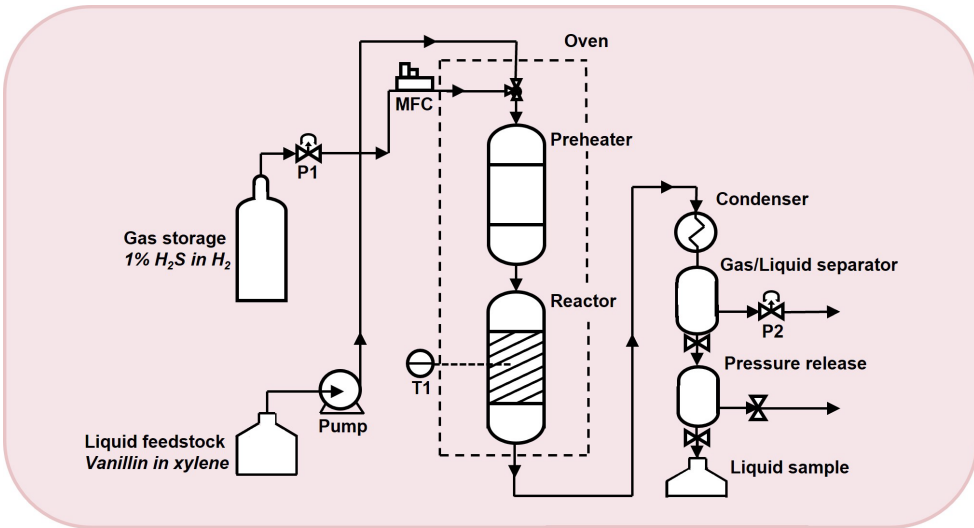

Figure 4.2. Overview of the continuous-flow reactor system used for investigations reported in **Papers I-III**. (Reproduced from **Paper I**)

The selectivity to cresol

The overall objective of performing HDO is ultimately to remove the oxygen. However, using xylene as the solvent for this investigation introduced challenges in evaluating the HDO experiments. The components in the resulting liquid samples were analysed using gas chromatography (GC) together with mass spectrometry (MS). Despite efforts to refine the GC-MS method, it was not possible to achieve a clear separation between the peaks for xylene, potential fully deoxygenated products, and possible saturated products (e.g., toluene and methylcyclohexane). Therefore, the evaluation of the impact of the experimental conditions focused on the selectivity to cresol.

4.2.2 Verification of setup and determination of optimal conditions

Verification of the constructed continuous fixed-bed reactor system was carried out using response surface methodology (RSM) and analysis of variance (ANOVA). For this investigation, employing RSM and ANOVA as statistical tools was considered advantageous compared to the conventional experimental one-factor-at-a-time approach (for example, initially changing the temperature stepwise, followed by adjusting the pressure in subsequent steps).

To gain a true understanding of the optimal conditions for a particular catalyst (in this case, the original Ni–Mo/δ-Al_2O_3 catalyst) for a defined outcome, it is essential to investigate the entire parametric range. The main advantage of this approach lies in the ability to study the impact of process parameters across a defined range with a reduced number of experiments. Additionally, this method allows for the determination of whether parameters influence the results individually or in combination [76]. It also enables the generation of regression models that represent the full parametric range explored in the investigation [77]. These models facilitate the identification of the optimal conditions for the desired outcome.

As presented in **Paper I**, a statistically significant model was generated based on the performed HDO experiments. This model represented the resulting selectivity to cresol for the constructed experimental setup over the entire investigated parametric range (i.e., between 250–350 °C, 3–9 bar(g), and 15–35 h^{-1}). It was established that temperature and pressure were the dominant parameters affecting the selectivity to cresol. The space velocity only showed an impact on selectivity in combination with temperature. Pressure was also confirmed to affect the selectivity to cresol in combination with temperature. These combined effects are presented as three-dimensional surface graphs in Figure 4.3. The optimal conditions for maximizing selectivity to cresol were determined to be at a temperature of 314 °C, using a pressure of 5 bar(g), and 35 h^{-1} in weight hourly space velocity (WHSV) [78].

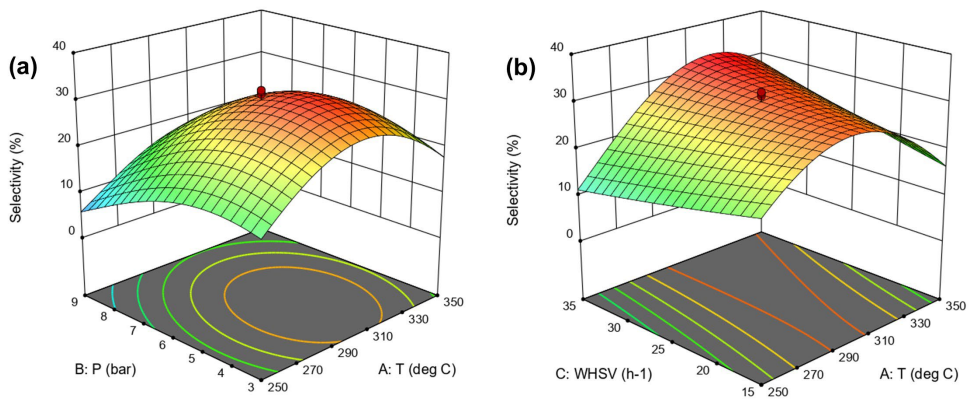

Figure 4.3. Regression model-based representative three-dimensional graphs for the resulting response (selectivity to cresol) with respect to (a) pressure (P) versus temperature (T), and (b) weight hourly space velocity (WHSV) versus temperature (T). Determined using the Ni–Mo/δ-Al_2O_3 catalyst. (Reproduced from **Paper I)**

4.3 The effect of using dopants

In the previous Section 4.2, the Ni–Mo/δ-Al_2O_3 catalyst was demonstrated to be active for the HDO of vanillin. The effect of the process parameters was investigated, and optimal conditions for achieving the highest selectivity to cresol with this catalyst were identified. These optimal conditions were subsequently applied in the studies presented in **Papers II** and **III**, from which the key findings are summarized in this section. Both papers address the strategy of modifying the support (as discussed in Chapter 3) by implementing a pretreatment step for δ-Al_2O_3 and introducing dopants before the impregnation of the active metals. The research described in these papers was conducted to determine whether including this pretreatment step during Ni–Mo catalyst synthesis is advantageous with respect to its performance in the HDO process.

Paper II represents the start of the core of this research project, and answers the first research question:

> RQ1: Is it advantageous to impregnate the support with La and Ce simultaneously, prior to heat treatment at 1100 °C?

As reported in **Paper II**, the effect of varying the availability of sulfur, both during the activation of the catalysts and/or during the HDO process, was also investigated. This topic is discussed further in Section 4.3.2.

However, isolating the true value of adding the dopants was limited within the scope of the investigation reported in **Paper II**. The work described in **Paper II** addressed the comparison between Ni–Mo catalysts supported on δ-Al_2O_3 that had either been pretreated and impregnated with 1 wt% of each La and Ce, simultaneously, or not. Therefore, several other factors (e.g., the heat exposure and resulting different phases of the Al_2O_3), not explicitly related to the use of the dopants, could have been the dominant reason for the outcome. As a progression from these insights, the second research question was formulated:

> RQ2: Is it advantageous to vary the amounts of La and Ce added to the support and the impregnation order of such, prior to heat treatment at 1100 °C?

The work related to answering the second research question, as reported in **Paper III** also considered the possibility of tuning the textural properties of the Al_2O_3. In the following sections, the key findings related to understanding the effect of the pretreatment, subject in Section 4.3.1, including the impact of the dopant amounts and impregnation order, whereas the evaluation of the different Ni–Mo catalysts' performance in the HDO experiments, covered in Section 4.3.2, are presented.

4.3.1 Understanding the effect of the pretreatment

To better understand the reasons for the observed differences in the HDO process, the properties of the various supports and, ultimately, the catalysts were evaluated using different characterization techniques (N_2-physisorption, XRD, NH_3-chemisorption, NH_3-TPD, and H_2-TPR as presented in Chapter 3). The key findings related to the effects of heat treatment, amounts of the dopants, and impregnation order on catalyst characteristics are presented and discussed below.

The effect of the heat treatment

As outlined in Chapter 3 (Section 3.1.1), the main purpose of implementing the pretreatment step for δ-Al_2O_3 (including heat treatment at 1100 °C) was to increase the pore diameter. Impregnating the La and Ce precursors before this heat treatment aimed to hinder sintering. In order to investigate the theory of this modification strategy, XRD and N_2-physisorption analysis were performed.

In **Paper II**, a phase transformation of Al_2O_3 from the designated δ- to the θ-phase was confirmed using XRD. The designated phase refers to the dominant phase (> 50% of the sample) as determined by Rietveld refinement [70]. The observed and calculated diffraction patterns are shown in Figure 4.4.

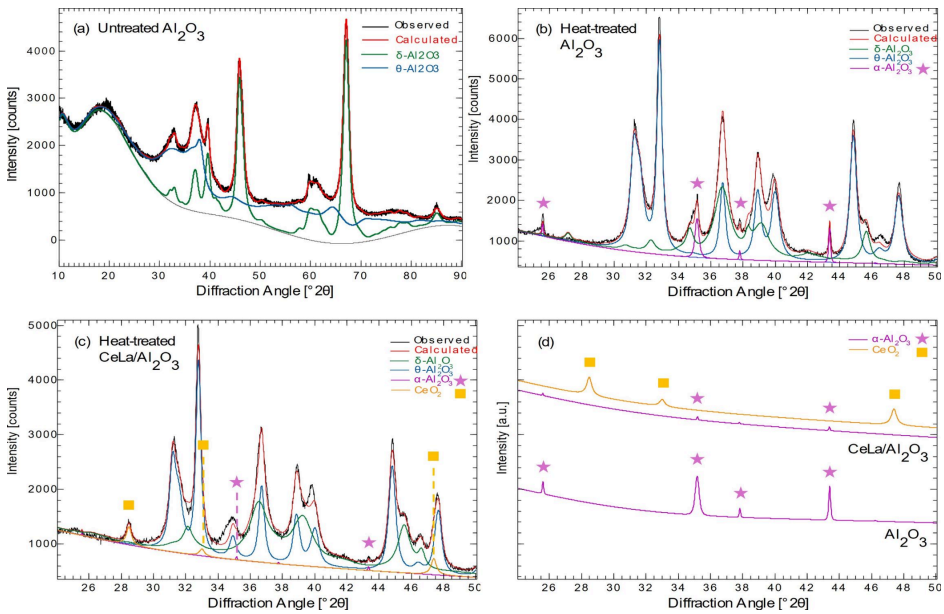

Figure 4.4. Observed and calculated diffraction patterns (using Rietveld refinement) from XRD analysis for (a) untreated Al_2O_3, (b) heat-treated Al_2O_3 (at 1100 °C), (c) heat-treated doped Al_2O_3 (simultanous impregnation with 1 wt% La and Ce prior heat treatment at 1100 °C), and (d) diffraction peaks dedicated to α-Al_2O_3 and CeO_2 from patterns in (b) and (c). (Reproduced from **Paper II**)

In addition, the increase in the pore diameter was confirmed after measuring the pore diameter of both the original and the heat-treated Al_2O_3 samples. In both **Papers II and III**, it was also suggested that impregnating δ-Al_2O_3 prior to the heat treatment with La and Ce hinders sintering, as the increase in pore diameter was relatively greater compared to the loss in surface area for this sample in relation to the heat-treated Al_2O_3 sample. The results from the performed N_2-physisorption are presented in Table 4.1.

Table 4.1.
Textural properties measured for the Al_2O_3 samples and the doped samples (impregnated simultaneously with 1 wt% of each La and Ce, respectively) after being treated at different temperatures. (Data from **Papers II** and **III**)

Parameter	Paper II			Paper III		
Sample	Al_2O_3	Al_2O_3	Doped	Al_2O_3	Al_2O_3	Doped
Temperature [°C]	Ambient	1100	1100	Ambient	1100	1100
Pore diameter (PD) [nm]	22	24	28	22	27	29
Surface area (SA) [m^2/g]	115	66	65	118	74	68
Ratio PD/SA	0.19	0.36	0.43	0.19	0.36	0.43

The effect of varying the amount of the dopants and the impregnation order

The findings presented in **Paper II** indicated that the use of the dopants (1 wt% impregnated simultaneously prior to heat treatment) resulted in a relatively greater increase in the pore diameter compared to the heat-treated Al_2O_3 sample (Table 4.1). This insight contributed to speculation about whether the pore diameter could be maximized by varying the amounts of the dopants, which led to the formulation of the second research question (RQ2). This was initially investigated in order to establish the formulations used as supports for catalysts evaluated for the HDO process in **Paper III**. The decision to investigate the effect of varying the amounts between 0–5 wt% for each metal, respectively, was based on results presented in the literature [59, 60]. Loadings between 2–8 wt% of Ce have been demonstrated to improve dispersion of a Ni–Mo/γ-Al_2O_3 and the catalytic performance for HDO of guaiacol [59]. Low loadings of La have been reported to be of particular interest for improving HDO over a Pt/γ-Al_2O_3 catalyst [60].

Additionally, the findings in **Paper II** contributed to speculation about whether the dopants had a combined and/or separate effect on the pore diameter. These speculations arose from the discovery that clusters of CeO_2, large enough to generate diffraction in the XRD analysis, were formed on the surface of the Al_2O_3, whereas no oxide of La was found. Thus, it was suggested that the dopants had a separate effect on the pore diameter and on the preservation of the surface area (that is, the hindering of sintering).

Therefore, it was also suggested that the order in which the dopants were impregnated could influence the ability to adjust the textural properties of Al_2O_3 during the pretreatment step. Consistent with findings from **Paper II**, which indicated that La was the dominant metal for hindering sintering (as CeO_2 clusters were detected via XRD), it was decided that La should be impregnated first, followed by Ce. Furthermore, a similar study emphasized that the order of La affects the performance of a Ni–Cu/Al_2O_3 catalyst used in the HDO process. While the impregnation order of Ce was not an affecting factor, it was stressed that La should be impregnated in an initial step for improved performance [61]. The interest of investigating whether it makes a difference if the Ce precursor was calcined at 500 °C instead of 1100 °C (for separate impregnation of the dopants) was also based on the detection of CeO_2 clusters on the surface in **Paper II**. Increased agglomeration of the metals is expected at higher calcination temperatures, and the idea of using 500 °C was therefore to reduce the risk of cluster formation.

In the work reported in **Paper III**, all of the underlying speculations that contributed to the formulation of the second research question (RQ2) were addressed and answered using various methods. Once again, RSM and ANOVA were advantageously applied (as described in Section 4.2.2) to analyse the impact over the entire range of dopant amounts (0–5 wt% of each dopant).

The pore diameter and surface area of the various pretreated samples were determined using N_2-physisorption and XRD to reveal differences in crystal structures. These methods confirmed that the pore diameter of pretreated Al_2O_3 is influenced by both the amounts of dopants and the order in which they are impregnated. Increased amounts of La were confirmed to increase the pore diameter, regardless of the impregnation approach (simultaneous or separate). A combined effect of the dopants on pore diameter was only confirmed when they were added together. Additionally, when aiming to maximize the pore diameter while still preserving a high surface area, it was proposed that minor amounts of Ce should be added only if the dopants were impregnated together.

Regardless, results from the N_2-physisorption analysis of the samples indicated better preservation of the surface area in relation to the increase of the pore diameter when the dopants were impregnated prior to the heat treatment. Additionally, the temperature at which the Ce was calcined affected the size of the CeO_2 crystals. For the samples containing Ce, relatively broader diffraction peaks were observed when Ce was calcined at 500 °C compared to 1100 °C. Broader peaks indicate smaller crystals, suggesting the formation of smaller CeO_2 crystals when a calcination temperature of 500 °C is used. The key findings are summarized and illustrated in Figure 4.5.

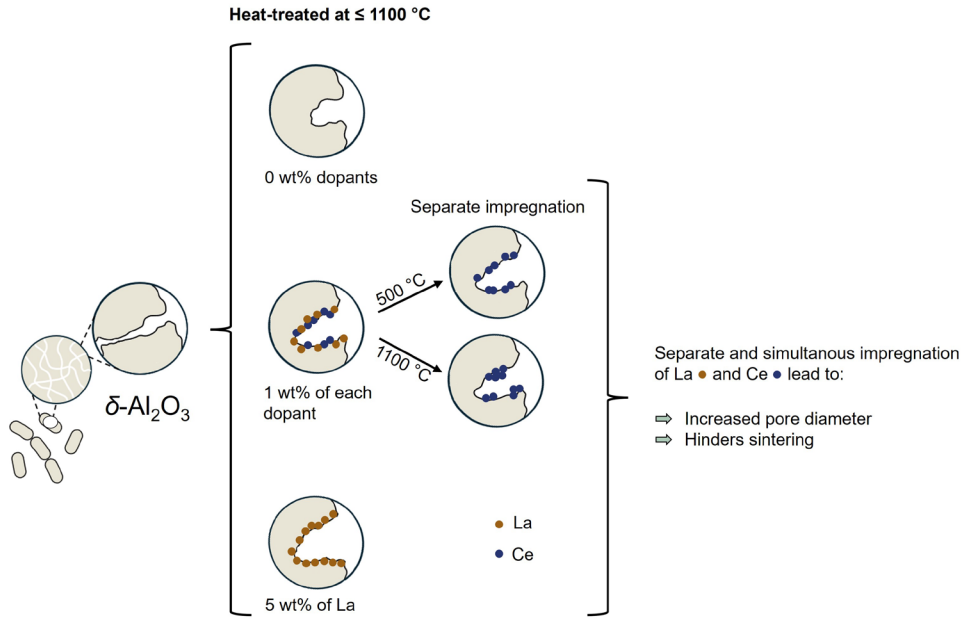

Figure 4.5. Illustration summarizing the main findings presented in **Paper III** regarding the effect of impregnating Al_2O_3 with varying amounts of La and Ce, as well as the order of impregnation, prior to heat treatment up to 1100 °C.

The effect on catalyst characteristics

The findings presented in **Papers II** and **III** indicate that the pretreatment affects the characteristics of the catalyst. The key findings are related to the differences in their reducibility. The original Ni–Mo/δ-Al_2O_3 catalyst, as described in **Paper II**, exhibits two main reduction regions at approximately 380 °C and 750 °C. These regions did correspond well with the reduction behavior of Ni–Mo catalysts supported on Al_2O_3 reported in the literature and were attributed to the reduction of Mo^{6+} to Mo^{4+} and Mo^{4+} to metallic Mo, respectively [79]. As reported in **Papers II** and **III**, corresponding reduction regimes were obtained for the various pretreated Ni–Mo catalysts as well. The H_2-TPR profiles, reported in **Paper III**, are shown in Figure 4.6. However, several differences were also observed. The relatively higher reduction temperatures of Mo^{6+} to Mo^{4+} observed for the doped catalysts were speculated to result from increased metal dispersion. Additionally, two peaks in the reduction regime between approximately 400 and 500 °C were observed, which were inferred to correspond to the reduction of polymeric and well-dispersed Mo species [80, 81]. Ni–Mo catalysts supported on Al_2O_3 doped with 5 wt% La (Figure 4.6a) were suggested to possess a higher ratio of polymeric Mo^{6+} compared to if 1 wt% La were impregnated (Figure 4.6b). Fewer interactions between Mo and the Al_2O_3 were also speculated to be a result of the pretreatment and the use of the dopants.

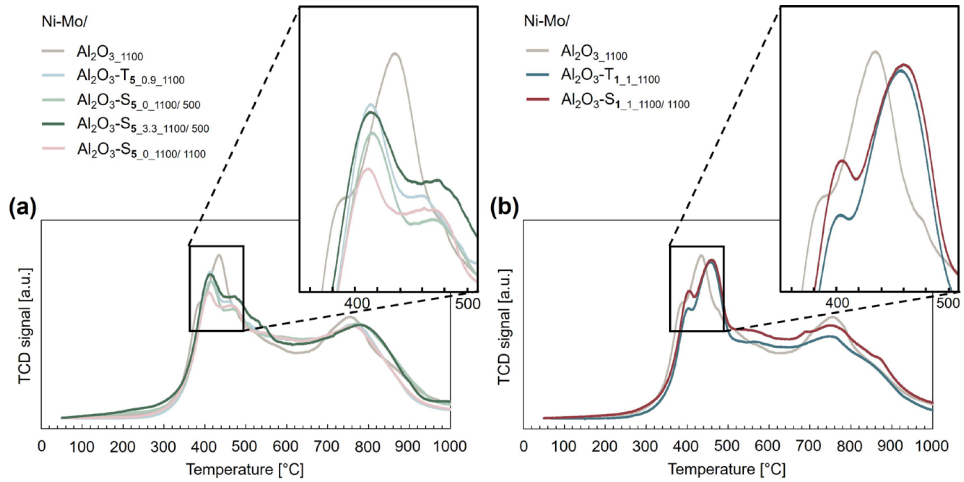

Figure 4.6. H_2-TPR profiles of the different Ni–Mo catalysts supported on treated Al_2O_3, divided between (a) and (b) depending on the amount of La, were (a) 5 wt% and (b) 1 wt%. The treated supports are denoted with 'T' and 'S' representing whether the dopants have been impregnated together ('T') or separately ('S'). The subscripts present the impregnated amount (wt%) of each La and Ce, respectively, together with the temperatures (°C) at which the treatment was performed. For comparison, Al_2O_3 treated at 1100 °C is also added in both (a) and (b). (Adapted from **Paper III**)

4.3.2 Evaluation of the performance in the HDO process

To ensure continuity with the previously established results reported in **Paper I**, and to address the first two research questions (RQ1 and RQ2), the same setup for the HDO experiments was used for the investigations reported in both **Papers II** and **III**. The optimal conditions determined for the original Ni–Mo/δ-Al_2O_3 catalyst (i.e., T = 314 °C, p = 5 bar(g), and WHSV = 35 h^{-1}) were applied throughout these investigations.

Additionally, the same analytical instrument (GC-MS) and method used in **Paper I** were employed to analyse the liquid products in these investigations. However, for these investigations, the gas composition at the outlet was also analysed using a GC instrument equipped with a flame ionization detector. Both the liquid products and the gas outlet were determined to enable evaluation of the propensity for direct HDO over the different catalysts used in **Papers II** and **III**. The assessment was based on the proposed reaction pathways presented in Figure 4.7. The reaction pathways were established in accordance with reports found in the literature [58, 73, 75, 82].

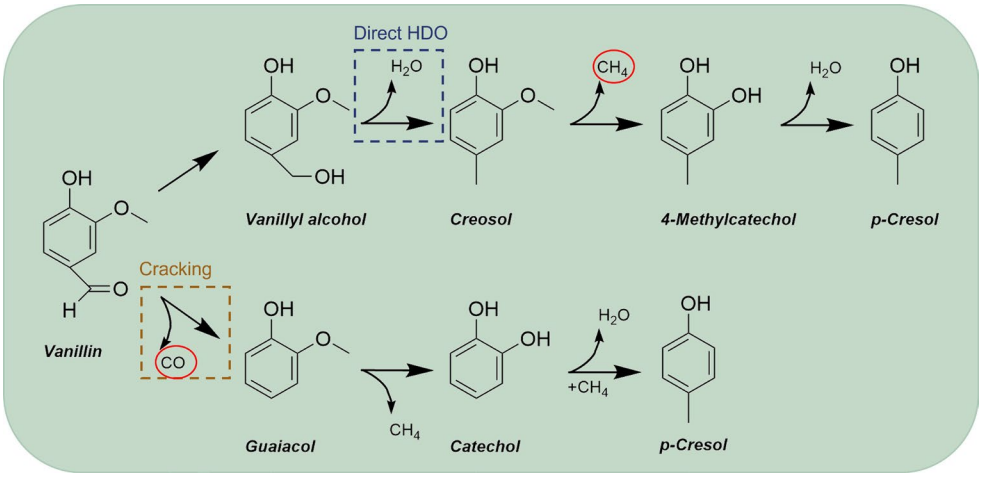

Figure 4.7. Proposed deoxygenation reaction pathways of vanillin to cresol. The defined reaction pathways applied herein are marked (direct HDO and cracking), whereas the gas products of CH_4 and CO, used for discussion in this section, are marked in red. (Adapted from **Paper II)**

Key findings from the work reported in these two papers are presented and discussed in this section. The discussion is divided into two parts: the effect of co-processing sulfur (as reported in **Paper II**) during the HDO experiments, and subsequently the effect of the dopants (as reported in **Paper III**). This division was chosen because the findings from co-processing sulfur were applied in the work conducted for the investigation reported in **Paper III** (and **Paper IV**).

The effect of co-processing sulfur

The work reported in **Paper II** also included HDO experiments in which the catalysts were activated (i.e., reduced) in situ in either pure H_2 or 1% H_2S (in H_2) prior to the experiments, and subsequently co-processed with a gas feed of either H_2 or 1% H_2S (in H_2) during the experiments. The relative ratios of the defined products (according to the reaction pathways proposed in Figure 4.7) that were formed during the different HDO experiments are presented in Figure 4.8.

The results showed that, regardless of the catalyst, sulfur needs to be co-fed either during activation of the catalyst or co-processed in the gas-feed. If sulfur was not co-fed, the conversion of vanillin was decreased to 88% after 8 hours, compared to remaining close to 100% when sulfur was included. It was further speculated whether activation with or without sulfur is more advantageous, provided that sulfur is co-fed during the reaction. The selectivity to cresol tended to be the highest for both catalysts when the activation was performed using only H_2. However, within the framework of this investigation, the obtained characterization results were not sufficient to explain the observed outcomes in the HDO experiments. Nevertheless, the findings provided confidence that the activation of the catalyst could be

performed ex-situ under pure hydrogen reduction conditions (using only H_2), while still ensuring an active catalyst if sulfur was added during the process. This enabled that the activation, and experiments could be done using different set-ups, which was considered beneficial from a practical and time perspective. This finding was implemented in the investigations presented in **Papers III** and **IV**, in which the catalysts were activated in 100% H_2 ex-situ.

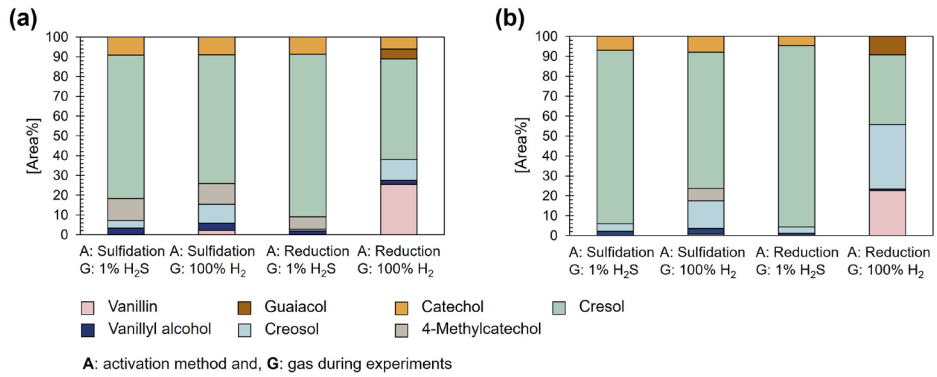

Figure 4.8. Relative ratios of the defined products detected in collected liquid samples from the different hydrotreatment experiments (performed as presented in **Paper II**, at 314 °C, using a pressure of 5 bar(g) and a weight hourly space velocity of 35 h^{-1}) over (a) the original Ni–Mo/δ-Al_2O_3 catalyst and (b) the Ni–Mo catalyst supported on Al_2O_3 impregnated with 1 wt% of each La and Ce, simultaneously, prior to heat treatment at 1100 °C. The results are for samples collected during 30 minutes prior to the experimental set time (8 hours). The activation method, denoted as A, is defined as sulfidation (using 1 % H_2S in H_2) or reduction (using 100% H_2). The used gas during the experiments (1 % H_2S in H_2 or 100% H_2) is denoted as G. (Adapted from **Paper II**)

The effect of the amounts of the dopants

All the research questions were formulated to evaluate whether the changes in catalyst preparation were advantageous for direct HDO and prolonged activity. This is a complex matter, given the limited amount of data, and therefore, results can only be discussed to a certain level of confidence. In **Paper II**, the assessment of whether the pretreated doped catalyst was more prone to direct HDO compared to the original Ni–Mo/δ-Al_2O_3 catalyst was based on evaluating the ratios of CH_4/CO formed during the HDO experiments. The data presented in **Paper II** showed a higher CH_4/CO ratio when the experiments were conducted with the pretreated doped catalyst, compared to the Ni–Mo/δ-Al_2O_3 catalyst. Additionally, prolonged activity was discussed in relation to the amount of carbon deposition on the used catalysts. Compared to the Ni–Mo/δ-Al_2O_3 catalyst, the pretreated doped catalyst exhibited relatively less carbon deposition. Based on the presented data, it was concluded that the doped catalyst was more prone to direct HDO, and a prolonged activity was anticipated. However, the results and discussion were limited, and

several other aspects were not discussed in **Paper II**, which could have added a higher level of certainty to the conclusions.

When considering the reaction pathway presented in Figure 4.7, it is possible to use the ratio of CH_4 to CO in order to determine which pathway is more prevalent. However, it remains a ratio, and if the conversion had not been close to 100%, or if the product distribution had been different, for example, forming more catechol and 4-methylcatechol compared to guaiacol and cresol, the ratio could have shifted and affected the conclusions. In this case, no such difference was observed for the experiments with sulfur, and the results were considered accurate at the time. Nevertheless, evaluating the selectivity to cresol based on the ratio of formed CH_4 and CO is more precise. Additionally, using carbon deposition on the used catalysts to predict a possible prolonged activity is complicated. Discussion related to the number of sites and how many times each site has been catalytically used is relevant to determine whether the catalyst remains active for a longer period or not [21].

In the work reported in **Paper III**, these insights were addressed, and the obtained data were evaluated accordingly. The selectivity per ratio of CH_4/CO and the carbon deposition determined for the used catalysts, together with the measured acidity of the fresh catalysts, are presented in Figure 4.9. These findings also demonstrated the tendency that simultaneous impregnation of the dopants (1 wt% of each) prior to the pretreatment step is advantageous for achieving a higher propensity for direct HDO compared to heat-treated Al_2O_3 (in similarity with the results reported in **Paper II**). Nevertheless, the main results indicated that lower amounts of dopants (1 wt%), either by adding them simultaneously or separately, were beneficial. Lower amounts of carbon deposition were suggested over these catalysts, compared to if 5 wt% La had been impregnated (Figure 4.9b).

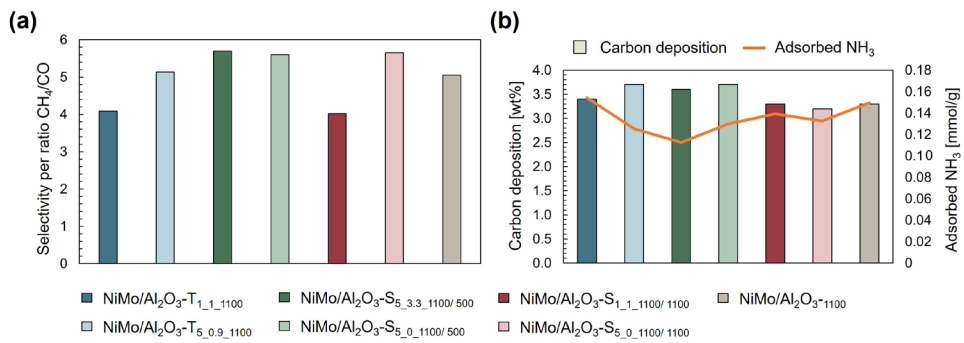

Figure 4.9. Results related to the different hydrotreatment experiments (performed as presented in **Paper III**, at 314 °C, using a pressure of 5 bar(g) and a weight hourly space velocity of 35 h^{-1}), presenting (a) the selectivity to cresol per CH_4/CO, and (b) the carbon deposition on the used Ni–Mo catalysts together with the total acidity for each fresh catalyst. The treated supports are denoted with 'T' and 'S' representing whether the dopants have been impregnated together ('T') or separately ('S'). The subscripts present the impregnated amount (wt%) of La and Ce, respectively, together with the temperatures (°C) at which the treatment was performed. (Adapted from **Paper III**)

4.4 The effect of using promoters

In this section, insights related to the work presented in **Paper IV** are described. This work was also framed as a progression of the findings gained after addressing the first research question (**Paper II**) and demonstrating the potential of pretreating the support. However, this investigation addressed the second possible modification strategy to reduce the risk of catalyst deactivation, namely, the addition of noble metals onto the doped Ni–Mo catalyst (i.e., the use of promoters, as discussed in Chapter 3). The third research question was formulated:

> RQ3: Is it advantageous to impregnate the doped Ni–Mo catalyst with a noble metal (Pd, Pt, or Ir)?

As described in Section 4.1, real lignin-derived oil was used in this investigation to gain a deeper understanding of the industrial prospects of the synthesized catalysts. Additionally, this investigation was framed to address the debate regarding the disadvantage of using noble metal-based catalysts for the HDO of lignin-derived oils due to their sensitivity towards sulfur. The HDO experiments were performed either without or with co-processing sulfur (dimethyl disulfide, DMDS, was used as the sulfur agent). Section 4.4.1 describes the evaluation performed to understand the underlying reasons for the observed differences in the HDO experiments, and the key findings from the experiments are summarized in Section 4.4.2.

4.4.1 The impact of the noble metals on catalyst characteristics

The different noble metals (Pd, Pt, and Ir) were impregnated in a subsequent step onto the pretreated, doped Ni–Mo catalyst (simultaneous impregnation of 1 wt% of each dopant, as used in **Paper II**). Several characterization techniques were employed to understand the impact of adding these metals. Catalyst morphology, acidity, and reducibility were evaluated using N_2-physisorption, SEM-EDX, XRD, NH_3-chemisorption, pyridine-FTIR spectroscopy, and H_2-TPR, respectively.

The most pronounced effect of impregnating the different noble metals was observed in their reducibility behaviour. The reducibility behaviour of these catalysts is assessed from their TPR profiles, presented in Figure 4.10. As previously discussed in Section 4.3.1, the Ni–Mo catalyst is reduced over two temperature regimes, at approximately between 400–500 °C and 750 °C. These reduction regimes correspond to the reduction of Mo^{6+} to Mo^{4+} and Mo^{4+} to the metallic state [79]. However, the pretreatment and use of the dopants were found to affect the ratio between polymeric and dispersed Mo^{6+} (Figure 4.6). In Figure 4.10, the polymeric Mo^{6+} is observed as a shoulder at approximately 400 °C in the TPR profile for the doped reference catalyst. Upon addition of the different noble metals, a change in reducibility was observed for both the polymeric and the dispersed Mo^{6+}. Both the

shoulder and the main peak, observed for the reference doped Ni–Mo catalyst at 400 °C and 480 °C, respectively, tended to be shifted to lower temperatures for the catalysts containing noble metals.

These observations were proposed, based on results found in the literature, to be due to the noble metal facilitating the reduction of Mo^{6+} [80]. In the profiles for the catalyst with Pd and Ir (Figure 4.10), the peaks observed at approximately 270 °C and 350 °C, respectively, were assigned to the reduction of Mo^{6+}, and the peaks at 100 °C and 210 °C were assigned to the corresponding noble metal, respectively [83–85]. For the catalyst with Pt, a relatively increased promotional effect in this regard was suggested compared to Pd and Ir. In addition, only one peak below 300 °C was observed in the profile for the Pt catalyst (at approximately 200 °C), and the hydrogen consumption was speculated to be higher than only corresponding to the reduction of Pt.

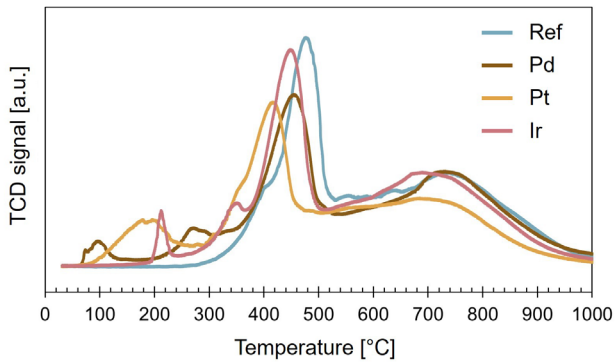

Figure 4.10. H_2-TPR profiles of the different catalysts used in work reported in **Paper IV**, including the reference (Ref) doped Ni–Mo/Al_2O_3-$T_{1\text{-}1\text{-}1100}$ catalyst (supported on Al_2O_3 impregnated with 1 wt% of each La and Ce, simultaneously, prior heat treatment at 1100 °C), and corresponding catalysts with Pd, Pt, and Ir. (Adapted from **Paper IV** with permission from the Royal Society of Chemistry)

Another evident difference between the doped reference Ni–Mo catalyst and the doped Ni–Mo catalyst with noble metals was observed through the pyridine-FTIR analysis. As described in Chapter 3 (Section 3.3), the NH_3-chemisorption only provides data on the total amount of acid sites, whereas the pyridine-FTIR allows for distinguishing the nature of the acid sites (electron-accepting sites, i.e., Lewis acid sites, and proton-donating sites, i.e., Brønsted sites) [86].

Therefore, with the opportunity to perform pyridine-FTIR as part of this investigation, it was considered interesting to understand the possible influence of noble metal addition on this ratio. However, the results only confirmed what had been proposed in the literature. Hydroxyl groups (-OH groups) located on the Al_2O_3 surface are recognized to hold both Brønsted sites characteristics and to be potential

anchoring sites for noble metal impregnation [86–88]. This was also reflected in the results gained from the pyridine-FTIR. The doped reference Ni–Mo catalyst contained a higher amount of Brønsted acid sites compared to the doped Ni–Mo catalysts with noble metals.

Apart from the differences detected in the TPR profiles and in the ratio between Brønsted and Lewis acid sites, no significant observations were made using the other characterization techniques (N_2-physisorption, XRD, SEM-EDX). Instead, it was proposed that the noble metals were impregnated equally.

4.4.2 Evaluation of the promoting effect for HDO

Given the numerous different compounds in the oils used in the HDO experiments, finding appropriate techniques for analysing the products was problematic. Time was spent deciding which techniques could be used to evaluate the oils, considering both reasonable timeframes and costs.

For example, gel permeation chromatography was considered to determine the size distribution of the resulting components. Karl Fischer titration was evaluated to measure the amount of H_2O formed during the HDO experiment. However, these techniques were ultimately rejected for their purpose. The lignin-derived oil had been dissolved in hexadecane; thus, analysing the size distribution of the resulting products proved troublesome. Overlapping peaks from monomers and hexadecane led to inaccuracies in the data. For the Karl Fischer titration, the biphasic nature of the liquid samples resulted in inaccurate measurements.

Instead, GC-MS was used to gain an understanding of the relative deoxygenation degree achieved with each catalyst. The relative abundance of non-oxygenated compounds compared to the feedstock is presented in Table 4.2.

Table 4.2.
Relative abundance (R.A.) of non-oxygenated compounds in liquid oils after hydrotreatment experiments (performed as reported in **Paper IV,** at 320 °C, and using an initial hydrogen pressure of 50 bar under batch conditions), comparing the addition of dimethyl disulfide (DMDS). The catalysts included are the reference (Ref) doped Ni–Mo/Al_2O_3-$T_{1\text{-}1\text{-}1100}$ catalyst (supported on Al_2O_3 impregnated with 1 wt% of each La and Ce, simultaneously, prior heat treatment at 1100 °C), and corresponding catalysts with Pd, Pt, and Ir. The R.A. of non-oxygenated compounds was determined to be 8% in the initial lignin-oil. (Data from **Paper IV)**

Catalyst	Without DMDS [%]	With DMDS [%]
Ref	28	51
Pd	30	37
Pt	30	44
Ir	30	37

It was demonstrated for all catalysts that the resulting liquid oils contained a relatively increased abundance of non-oxygenated compounds when DMDS was co-processed (Table 4.2). In addition, as presented in **Paper IV**, lower amounts of oxygenated phenols were detected in the resulting oils for all catalysts, compared to the feedstock. The feedstock contained 58 % oxygenated phenols, whereas the resulting oils contained 15–27 % and 2–10 % when DMDS was co-processed. A greater tendency toward direct HDO was proposed for all catalysts when DMDS was co-processed. The results indicated that the greatest removal of oxygen was achieved when the doped reference Ni–Mo catalyst was used. Additionally, the highest abundance of aliphatic compounds in the resulting oil was observed when this catalyst was employed in combination with DMDS co-processing. The feedstock and product oils collected in experiments using the reference doped Ni–Mo catalyst (supported on Al_2O_3 impregnated with 1 wt% of each La and Ce, simultaneously, prior to heat treatment at 1100 °C) are shown in Figure 4.11.

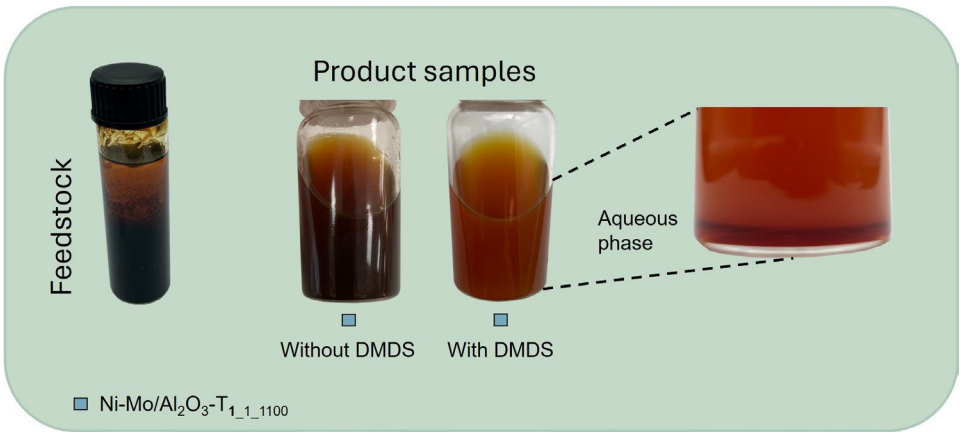

Figure 4.11. The feedstock and the collected product samples for the hydrotreatment experiments (**Paper IV**), either without or with co-processing dimethyl disulfide (DMDS), under batch conditions (at 320 °C, and using an initial hydrogen pressure of 50 bar), for when the reference doped Ni–Mo/Al_2O_3-$T_{1\text{-}1\text{-}1100}$ catalyst (impregnated with 1 wt% of each La and Ce, prior to heat treatment at 1100 °C) was used.

However, the evaluation of the carbon deposition on the catalyst suggested a possible positive effect from using Pt. As discussed in Section 4.3.2, it is important not only to measure the total amount of carbon deposition, but also to consider it in relation to the catalyst's activity and acidity. Therefore, the measured carbon deposition was plotted per the relative abundance of non-oxygenated compounds, and is shown in Figure 4.12. These results suggested a positive effect from the addition of the noble metals, particularly Pt, when sulfur is co-processed. Lower amounts of carbon deposition per relative abundance of non-oxygenated compounds were speculated to result from reduced polymerization.

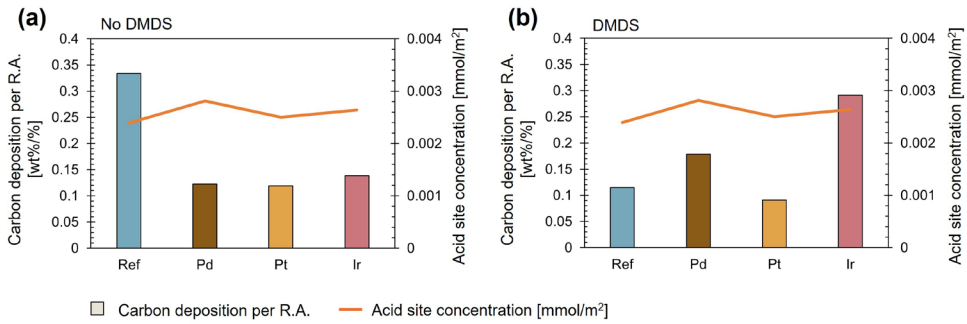

Figure 4.12. Carbon deposition detected on the used catalysts (from elemental analysis) per relative abundance (R.A.) of non-oxygenated compounds after performing hydrotreatment experiments, either (a) without dimethyl disulfide (DMDS), or (b) with co-processing DMDS. The determined total acid site concentration of the fresh catalysts is also plotted. The catalysts included are the reference (Ref) doped Ni–Mo/Al_2O_3-$T_{1\text{-}1\text{-}1100}$ catalyst (supported on Al_2O_3 impregnated with 1 wt% of each La and Ce, simultaneously, prior heat treatment at 1100 °C), and corresponding catalysts with Pd, Pt, and Ir. (Adapted from **Paper IV** with permission from the Royal Society of Chemistry)

4.5 The use of a graded catalyst-packed bed

Up to this point, insights from work reported in **Papers II**–**IV** indicated the potential of applying the pretreatment strategy of the Al_2O_3 that includes the use of the dopants. However, in the previous framed investigations, catalyst characteristics were evaluated in association with HDO experiments performed over a set time period. This limited the discussion on whether the pretreatment strategy was actually advantageous in the context of longer processing times, which was the primary overarching aim of including a pretreatment step for the original δ-Al_2O_3.

Additionally, during the research project, another challenge associated with the HDO process was identified. It was learned that the reactor is often plugged at the top of the catalyst bed due to carbon formation, which consequently leads to a stop in the process (continuous-flow process).

Therefore, in an attempt to address both these insights and to adopt the findings from **Papers II**–**IV**, a final research question was formulated:

> RQ4: Is it advantageous to have a graded catalyst-packed bed in which the support pretreatment is the altering factor between the catalysts used in the top layer?

For this investigation, as reported in **Paper V**, no time limit for the HDO experiments was set. Instead, the research question was addressed by evaluating how long the HDO experiments could last until a pressure drop was detected.

The work was framed to investigate whether the addition of a Ni–Mo catalyst supported on Al_2O_3 heat-treated at 1100 °C or 1250 °C, impregnated with La and Ce either together or separately, as the top layer in a catalyst bed would be advantageous for achieving longer times-on-stream. The amount of La and Ce was kept at 1 wt%, consistent with what was found to be most beneficial for the HDO process in **Paper III**. The overarching aim was to gain an understanding of whether increased temperature (1100 °C to 1250 °C) used during the pretreatment could result in more appropriate textural properties, allowing for the largest components in the lignin-derived oil to be deoxygenated prior to deeper HDO further down in the catalyst bed. It was speculated whether this could reduce the risk of plugging in the top of the bed.

The key findings related to the effect of the pretreatment are presented in Section 4.5.1, followed by the findings from the HDO experiments in Section 4.5.2.

4.5.1 The effect of the pretreatment temperature

In relation to performance in the HDO process, the advantages identified from including a heat treatment step of Al_2O_3, along with the use of La and Ce as dopants, have primarily been discussed based on insights gained from differences in structural characteristics (based on, e.g., H_2-TPR, NH_3-chemisorption, and NH_3-TPD).

Less discussion has focused on the textural properties. While pore diameters and surface areas have been evaluated in relation to the research questions and the pretreatments, the effect of these measured textural properties has not been discussed in detail in terms of their impact on the outcome of the HDO process. This perspective was addressed when evaluating data reported in **Paper V**. Additional efforts were made to evaluate data obtained from N_2-physisorption in association with pore size and volume distribution. Moreover, all the relevant Al_2O_3 samples were examined in this regard.

Compared to previous findings (reported in **Paper III**), the evaluation of Al_2O_3 samples used to assess the effects of pretreatment and dopants was limited. Only the original δ-Al_2O_3 and Al_2O_3 treated at 1100 °C (according to the heat treatment approach equivalent to if the dopants were impregnated together) were included. Al_2O_3 samples heat-treated at selected temperatures for this investigation (1100 °C and 1250 °C), in an equivalent sequence as if the dopants were added together or separately, were evaluated.

The pore shape of all Al_2O_3 samples was evaluated by analysing the obtained N_2-physisorption isotherms. According to the classifications defined by IUPAC, the original δ-Al_2O_3 and pretreated doped samples showed type IVa isotherms, which indicate a mesoporous structure. Additionally, the observed hysteresis loops

resembled H1-type loops, suggesting ink-bottle-shaped pores, regardless of the presence or type of dopants [65]. A simplified illustration of proposed ink-bottle-shaped pores is shown in Figure 4.13.

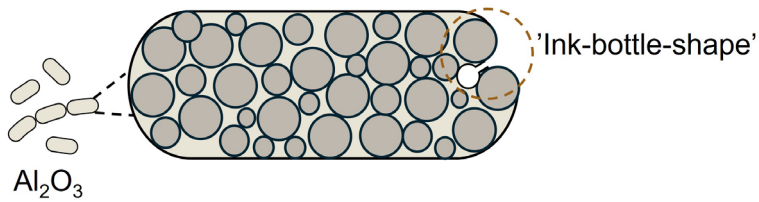

Figure 4.13 Illustration of an ink-bottle shape of the bulk Al_2O_3, including intraparticle mesopores.

However, samples treated at 1250 °C resulted in a significant loss in texture. Only possible micropores on the surface were proposed to remain for Al_2O_3 treated at this temperature. For the doped samples, while losing surface area, the pore diameter was determined to be ~25–33 nm (compared to ~10 nm for the treated Al_2O_3 samples), and thus, more interparticle pores were proposed to be preserved for these samples. All the samples treated at 1250 °C were confirmed by XRD to have transformed predominantly to the stable α-phase.

Furthermore, for the Ni–Mo catalysts, the key findings were observed when evaluating the pore volume distribution in relation to pore width. The pore volume distribution in relation to pore width for the different supports and catalysts is presented in Figure 4.14. A bimodal structure, resulting from impregnation of the active metals (Ni and Mo) onto the inner surface of pores with a certain pore diameter (width), and/or blockage of pores with a certain diameter, was proposed for the Ni–Mo catalysts supported on Al_2O_3 treated at 1100 °C (Figure 4.14a). The reason for not obtaining a bimodal structure of the Ni–Mo catalysts supported on Al_2O_3 treated at 1250 °C (only one main region for the pore volume distribution for these catalysts, as observed in Figure 4.14b), was proposed as a result of the low amount of pore volume of the support (10-fold lower amount compared to Al_2O_3 treated at 1100 °C). Instead, the increased amounts of pore volume for these catalysts, compared to their corresponding support (Figure 4.14d), were proposed as a result of clusters of the active metals, also causing measurable pore volume. Independent of the temperature of the heat treatment, the separate impregnation of La and Ce was proposed to result in catalysts with pore volume distributed in narrower pores.

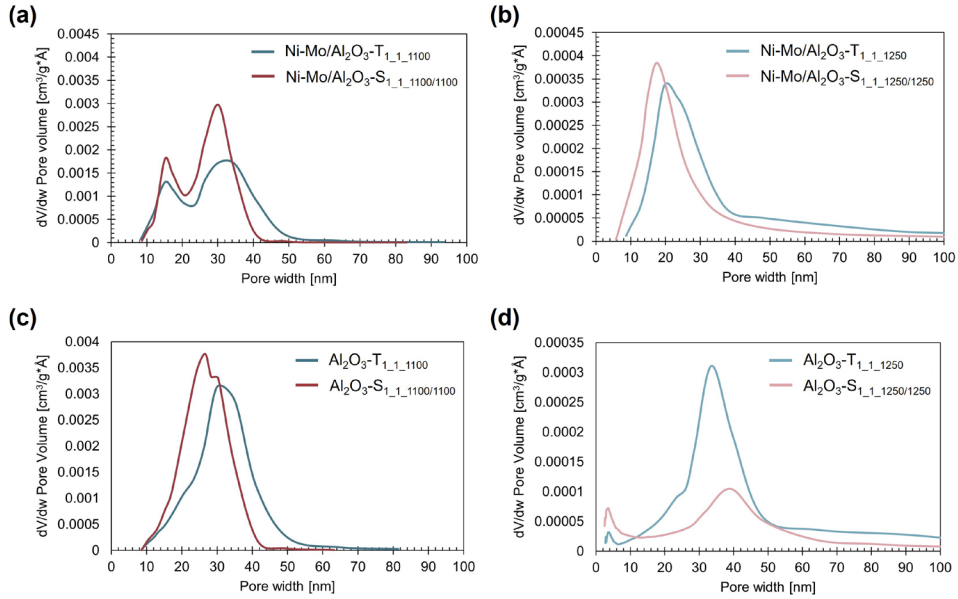

Figure 4.14. Pore volume distribution in relation to pore width determined for Ni–Mo catalyst supported on Al_2O_3 treated at (a) 1100 °C and (b) 1250 °C (with 10-fold lower values on the y-axis). Distribution determined for corresponding supports are in presented in (c) and (d). The treated supports are denoted with 'T' and 'S' representing whether the dopants have been impregnated together ('T') or separately ('S'). The subscripts present the impregnated amount (wt%) of La and Ce, respectively, and temperatures (°C) at which the treatment was performed. (Adapted from **Paper V**)

4.5.2 HDO of a lignin-derived oil under continuous-flow conditions

The experiments conducted to address the fourth research question (RQ4), as presented in **Paper V**, involved the hydrotreatment of lignin-derived oil (Lignol®, produced by RenFuel K2B AB). For this purpose, 30 wt% of Lignol® was dissolved in light gasoil and hydrotreated under continuous-flow conditions at 360 °C, using a pressure of 100 bar and a liquid hourly space velocity of 0.8 h^{-1}.

With the intention of enabling further investigation of the catalysts following the HDO experiments, specifically to examine possible structural changes and carbon deposition, the experiments were designed to be aborted when a pressure drop was detected. Removing the catalyst from reactors that have been used for HDO until the process completely stops due to plugging is practically difficult.

However, in the end, the catalysts used were deemed unsuitable for further evaluation, as the experiments continued until they were manually aborted. As a result, since the tests proceeded during hours when regular monitoring was not possible, the pressure drop was reached, on some occasions, during those periods. This resulted in inconsistent durations for the HDO experiments. Consequently,

variations in factors such as carbon deposition on the different catalyst surfaces could have arisen from differences in process times. Additionally, the shutdown and subsequent rinsing of the system prior to reactor removal were handled differently between some experiments. This was also speculated to interfere with the accuracy of the intended evaluation of the used catalysts. Instead, the investigation reported in **Paper V** was limited to evaluating differences in characteristics of fresh catalyst with respect to the set time-on-stream (defined as when the pressure drop was 0.2 bar), yields, and produced oil composition (volume ratios of paraffin, isoparaffin, naphthene, and aromatic compounds).

The most obvious finding was the differences in the time-on-stream. It was demonstrated that longer times-on-stream are achieved when the Ni–Mo catalyst used in the top was supported on Al_2O_3 treated at 1100 °C, compared to using Al_2O_3 treated at 1250 °C as the support. However, it was also demonstrated that impregnation of the La and Ce in separate steps is more beneficial for improving the process stability. The most successful experiment was achieved when the Ni–Mo catalyst, supported on Al_2O_3 treated at 1100 °C and impregnated with La and Ce in separate steps (Ni–Mo/Al_2O_3-$S_{1\_1\_1100/1100}$), was at the top of the graded catalyst bed. This experiment proceeded for 288 hours. The feedstock and the collected product oil samples (the initial and the last samples), as for the resulting times-on-stream for the different experiments, are shown in Figure 4.15.

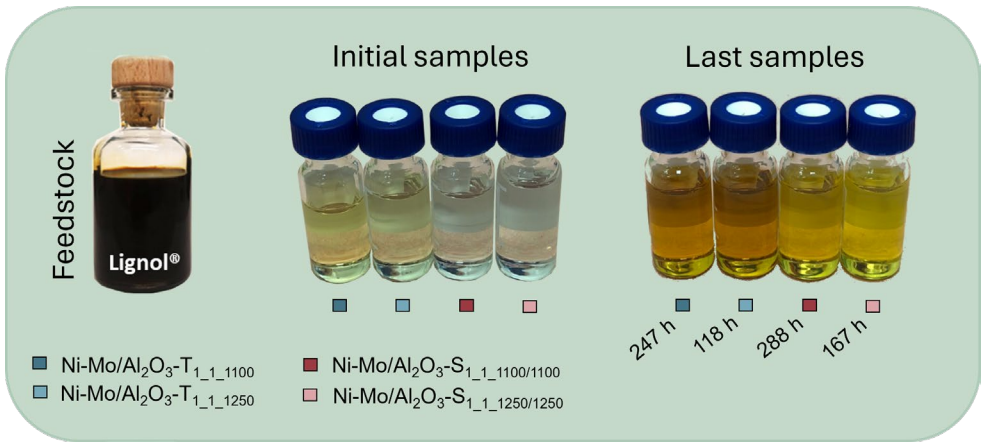

Figure 4.15 The feedstock, initial and last collected hydrocarbon sample for each hydrotreatment experiment (performed as reported in **Paper V**, at 360 °C, using a pressure of 100 bar, and a liquid hourly space velocity of 0.8 h^{-1}). The time-on-stream until a pressure drop of 0.2 bar was detected is also given. The treated supports are denoted with 'T' and 'S' representing whether the dopants have been impregnated together ('T') or separately ('S'). The subscripts present the impregnated amount (wt%) of La and Ce, respectively, and temperatures (°C) at which the treatment was performed.

Furthermore, tendencies of differences in oil composition between the collected oil samples during the HDO experiments, performed with Ni–Mo catalysts supported on Al_2O_3 treated at 1100 °C (Ni–Mo/Al_2O_3-$T_{1\_1\_1100}$ and Ni–Mo/Al_2O_3-$S_{1\_1\_1100/1100}$), were observed. Increased amounts of saturated compounds were observed in the product oil samples collected from experiments using Ni–Mo catalysts supported on Al_2O_3, impregnated with La and Ce in separate steps (Ni–Mo/Al_2O_3-$S_{1\_1\_1100/1100}$), compared to being impregnated together (Ni–Mo/Al_2O_3-$T_{1\_1\_1100}$). No such differences could, however, be established when the experiments were performed over the Ni–Mo catalyst supported on Al_2O_3 treated at 1250 °C. The resulting volume ratios of paraffin, isoparaffin, olefin, naphthene, and aromatic compounds in the collected product oils are presented in Figure 4.16.

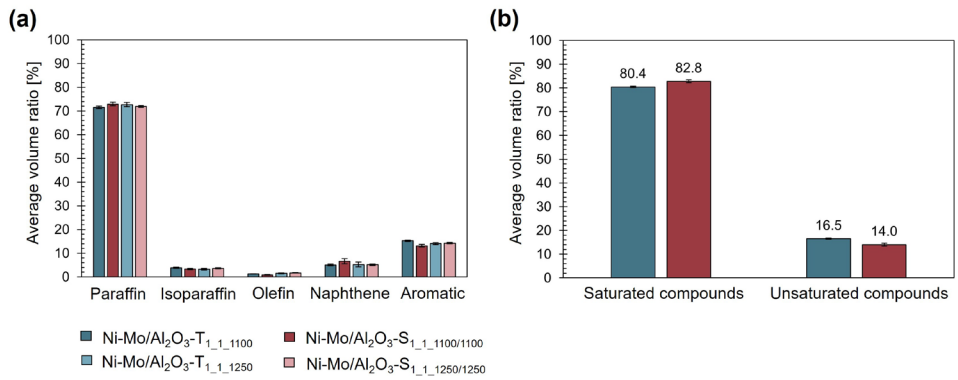

Figure 4.16. Average volume ratio of detected compounds divided into (a) paraffin, isoparaffin, olefin, naphthene, and aromatic compounds, and (b) total amount of saturated and unsaturated compounds, in the collected product oils over time for the hydrotreatment experiments performed using various Ni–Mo catalysts in the top layer of a graded catalyst bed. The treated supports are denoted with 'T' and 'S' representing whether the dopants have been impregnated together ('T') or separately ('S'). The subscripts present the impregnated amount (wt%) of La and Ce, respectively, and temperatures (°C) at which the treatment was performed. Experiments were conducted at 360 °C, using a pressure of 100 bar, and a liquid hourly space velocity of 0.8 h^{-1}. (Adapted from **Paper V**)

Both textural and structural properties were suggested to influence the catalytic performance in the HDO process, based on the findings presented above. The improved process stability over the Ni–Mo catalysts, supported on Al_2O_3 treated at 1100 °C, compared to the ones supported on Al_2O_3 treated at 1250 °C, was suggested as a result of the preserved texture of such. The low surface area and the low amount of acid sites, determined for the Ni–Mo catalysts supported on Al_2O_3 treated at 1250 °C, were suggested to negatively affect process stability. Instead, the difference in the achieved time-on-stream between those catalysts (and the ones supported on Al_2O_3 treated at 1100 °C) was attributed to the observed difference in their pore volume distribution. Pressure drop is not detected until carbon is deposited between catalyst particles [49]. More favourable porosity, allowing for

greater carbon deposition in intraparticle voids, prolongs the process stability. This was proposed as an affecting factor for achieving comparable prolonged time-on-stream for employing separate impregnation.

In addition, the differences in the product oil composition measured when Ni–Mo catalysts supported on Al_2O_3 treated at 1100 °C (Figure 4.16) were used, also contributed to suggesting that separate impregnation results in decreased risk for polymerization and, consequently, improved process stability. The increased amounts of saturated compounds in the product oil, collected when separated impregnation had been employed (using the Ni–Mo/Al_2O_3-$S_{1\_1\_1100/1100}$ catalyst), suggest improved hydrogenation capability of such a catalyst. It was speculated that an increased number of acid sites with intermediate strength, proposed for this catalyst, enhanced the hydrogenation capability. As a result, less polymerization was believed to occur, which in turn also could explain the more successful longer time-on-stream observed for the Ni–Mo/Al_2O_3-$S_{1\_1\_1100/1100}$ catalyst.

5 Conclusions

The development of an efficient catalyst for the HDO process of lignin-derived oils to liquid fuels is key to ensuring the advancement of its industrial implementation. The work described in this thesis offers strategies and insights into how characteristics of a Ni–Mo/δ-Al_2O_3 catalyst can be tuned for improved performance in this process. In particular, the work was dedicated to minimizing the risk for deactivation caused by carbon deposition on the catalyst surface, while increasing its selectivity for direct deoxygenation (oxygen removed as H_2O). The key findings were attributed to four research questions. The conclusions for each research question are presented below.

> Is it advantageous to impregnate the support with La and Ce simultaneously, prior to heat treatment at 1100 °C?

The findings indicate that it is advantageous to include a pretreatment step (impregnation of La and Ce precursors prior to heat treatment) of the δ-Al_2O_3 as part of the catalyst synthesis. Comparison between a common Ni–Mo/δ-Al_2O_3 catalyst and a Ni–Mo/Al_2O_3 catalyst doped with La and Ce demonstrated enhanced catalytic performance over the doped catalyst for the HDO process of a lignin model compound (vanillin). The relative improved performance is attributed to the increased selectivity to cresol, with a higher ratio for the removal of oxygen as H_2O compared to CO, and lower carbon deposition on the catalyst surface.

> Is it advantageous to vary the amounts of La and Ce added to the support and the impregnation order of such, prior to heat treatment at 1100 °C?

Depending on the desired result, it can be advantageous to vary the amounts of La and Ce precursors and the order in which they are impregnated. It is concluded that, with the intention of maximizing the pore diameter as a prerequisite to diminish diffusion limitations, high amounts La precursors should be impregnated prior to the heat exposure. Higher amounts of La prior heat exposure resulted in increased pore diameter (5 wt% as the highest tested amount), while Ce tends to improve the structural properties of the catalyst. However, in contrast, lower amounts of La tend to be more beneficial with respect to improving the catalytic performance of the Ni–Mo catalyst in the HDO process. High amounts of La (5 wt%) tend to affect the reaction pathway, causing higher carbon deposition per deoxygenation degree.

Lower amounts of the dopants (1 wt% of each metal) are concluded to be beneficial for the HDO process.

> Is it advantageous to impregnate the doped Ni–Mo catalyst with a noble metal (Pd, Pt, or Ir)?

The key findings demonstrated that the doped Ni–Mo/Al_2O_3 catalyst (simultaneously impregnated with 1 wt% of each La and Ce) promoted with Pt potentially can be advantageous for improving the performance in the HDO process of lignin-derived oils. Findings from the conducted HDO experiments show that the doped Ni–Mo/Al_2O_3 catalyst performs better, in relation to oxygen removal, compared to the catalysts with noble metals. However, the catalyst with Pt indicates less carbon deposition on the used catalyst surface, as determined by the relative abundance of non-oxygenated compounds. These findings are attributed to the proposed enhanced hydrogenation capability of such a catalyst. Thus, the potential advantage of adding Pt to the Ni–Mo/Al_2O_3 is inferred from a proposed prolonged activity of such.

> Is it advantageous to have a graded catalyst-packed bed in which the support pretreatment is the altering factor between the catalysts used in the top layer?

The framed investigation included the variation of the catalyst added in the top layer, which was varied depending on the pretreatment approach of the δ-Al_2O_3. Either the pretreatment entailed impregnation of La and Ce together or separate steps, and heat treatment at 1100 °C or 1250 °C. Findings from performing HDO of a lignin-derived oil demonstrated that separate impregnation is favorable compared to impregnating the dopants together. Enhanced textural properties for these catalysts are suggested to suppress the growth of carbon deposition between catalyst particles and, thus, improve process stability. Separate impregnation and heat treatment at 1100 °C was proven to be most advantageous. Findings also demonstrated improved hydrogenation capability for this catalyst, and a lower risk for polymerization is proposed using this catalyst.

In addition to key findings and conclusions related to the research questions, parallel investigations and discussions about sulfur dependency for Ni–Mo/Al_2O_3 catalysts are presented in the thesis. Nevertheless, within the set framework of this research project, the only conclusion drawn is the necessity of co-processing sulfur to maintain their activity. However, in accordance with the stated main advantage of using the Ni–Mo/Al_2O_3 for the HDO process of lignin-derived oils to liquid fuels (discussed in Chapter 2), this is not addressed as a concern but as beneficial.

6 Future work

The findings presented in this thesis demonstrate a Ni–Mo/Al_2O_3 catalyst doped with La and Ce, with the potential to contribute to the implementation of industrial HDO of lignin-derived oils to fuels. Certainly, this is an ongoing work, and several aspects need to be further considered for establishing its full potential. Here, proposed subjects of future research work are presented.

Firstly, it would be of interest to further validate the capability of the Pt–Ni–Mo/CeLa/Al_2O_3 catalyst. Findings showed that this catalyst may possess properties favourable for a prolonged activity in the HDO process. Confirming this by performing activity measurements would contribute to a more accurate assessment of its potential.

Secondly, sulfur influences the catalyst's performance. Generally, investigating the correlation between catalyst activity and sulfur availability could offer valuable insights into the catalyst's overall potential. Understanding the effect of the dopants in this aspect would also be valuable for guiding further catalyst optimization.

Thirdly, another relevant aspect that is essential to investigate for providing a true understanding of the catalyst's potential is its stability towards H_2O. This aspect was not thoroughly addressed within this thesis, but should be included in the assessment of its potential. This, as H_2O (the main product in the HDO process), is identified as problematic for the activity of the Ni–Mo/Al_2O_3 catalyst. Future studies should address this aspect and explore whether the use of the dopants mitigates the impact of H_2O.

Fourthly, evaluating the ease and feasibility of regenerating the catalyst would provide further insight into its industrial prospects. Understanding its potential for reuse would offer valuable information from both economic and environmental perspectives.

Finally, the advancement in the implementation of the HDO process of lignin-derived oils to fuels should continue to include joint efforts across various research fields. A coordinated approach that takes into account all elements, such as reactor design and life cycle assessment, would provide a more profound validation and argumentation for the feasibility and potential of implementing this process on an industrial scale.

7 References

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