Investigation of Alloy Catalysts for Conversion of Sustainable Energy

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PhD Thesis

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Version: PhD thesis in digital A4-format with no cover, handed in on 4th of January 2022 to the Technical University of Denmark.

Cover illustration (only on printed version): The "roof-top" of Europe. Photography taken by the author on the top of *Hochenhorn* facing south-west. The mountain peaks in the image are annotated in Figure A.1. The horn is situated on a ridge between the village of Kandersteg and Wiler, Switzerland. Neighbouring the horn on the same ridge is the "Lötchenpasshütte" offering bed-rest for travellers. The hut's energy-supply is based on 3.5 kW solar-panels on the facade and a 4 kW wind-turbine, where excess energy is stored in batteries and heated water, with water from their roof-placed water-collectors. Occasionally wood from the lower Lötschenhal is necessary due to prolonged weather conditions or peak usage from visitors. `https://www.loetschenpass.ch/en/`

Back-Cover illustration (only on printed version): Photography taken by the author on the top of *Hochenhorn* facing south. The mountain peaks in the image are annotated in Figure A.2.

Coat-of-arms: The Smitshuysen family coat-of-arms. The Smitshuysen family is a non-noble dutch-origin family, with traceable lineage back to the late middle ages. The lineage is broken around the 16th century, though this is explained by the rapid burning of church records among other things belonging to the catholic church at the time.

Preface

This thesis is submitted as a partial fulfilment of the degree of PhD in physics at the Technical University of Denmark (DTU). The work was carried out at the Section of Surface Physics and Catalysis (DTU Surfcat) at the Department of Physics (DTU Physics), and has been supervised by Associate Professor Christian Danvad Damsgaard and co-supervised by Professor Ib Chorkendorff. The work was carried out from 1st of September 2018 until 4th of January 2022 and has been funded by DTU Physics and partly funded by the Villum Foundation (V-Sustain, grant 9455). The research was carried out in collaboration with the National Centre for Nano Fabrication and Characterization at DTU (DTU Nanolab), Institute for Chemical Technology and Polymer Chemistry and Institute of Catalysis Research and Technology at Karlsruhe Institute of Technology, MaxIV Laboratory at Lund University, and the Department of Materials Science and Engineering at University of Pennsylvania.

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Abstract

This thesis presents research within development and characterisation of thermal heterogeneous catalyst for the reactions of methanol synthesis from CO_2, ethanol synthesis from CO, and propene oxidation to CO_2. The first two reactions are propositions for synthesising fuels from sustainable H_2 and captured CO_2, which is either used directly or preprocessed into CO. Propene oxidation is used as a model-reaction to investigate atomised platinum catalysts. In this research catalytic activity experiments, transmission electron microscopy and spectroscopy, X-ray diffraction and X-ray absorption have been used to assess and characterise the catalysts.
For the methanol synthesis from CO_2 ternary alloy catalyst Ni_2FeGa/SiO_2 has been optimised. The optimisation lead to the conclusion that a temperature of 550 C in H_2 during the formation of the nanoparticles from metal-nitrates is optimal for when the catalyst is subsequently used for methanol synthesis. Characterisation elucidated that this temperature is optimal for forming the alloy while at the same time avoiding sintering. Ni_2FeGa/SiO_2 was assessed in perspective to industrial grade $Cu/ZnO/Al_2O_3/MgO$, where it performs similarly at temperatures below 200 C, though Ni_2FeGa/SiO_2 has a lower selectivity towards methanol.
For the ethanol synthesis from CO, a ternary alloy catalyst, namely $CoCu_2Ga/SiO_2$, was conceived and developed. These metals are carefully selected: cobalt and copper because literature shows that the combination of the two will efficiently catalyse ethanol synthesis, and gallium to offer stability to the alloy. Different weight-loadings of the $CoCu_2Ga$ on the SiO_2 was synthesised and tested. Having 3.5% weight of $CoCu_2Ga$ did produce ethanol and in larger amounts, methanol and methane. This catalyst was compared with purchased Rh/C, which made mostly methane with smaller amounts of acetaldehyde, methanol and ethanol. Characterisation showed that ternary alloyed nanoparticles were in fact formed in the $CoCu_2Ga/SiO_2$ catalysts following a synthesis by reduction of metal-nitrates at 620 C in H_2. By a combination of *in situ* X-ray methods and microscopy with spectroscopy it has been shown that small cobalt-rich particles segregates from the ternary alloy when heated in reaction conditions.
Finally a catalyst comprised of only 0.05% weight platinum supported on $MgAl_2O_4$ was tested for propene oxidation reaction. This catalyst was found to be very catalytically active when comprised of small nano-sized clusters and inactive when the platinum atomised into single atomic sites. These states was found to be reversibly changed by heating at above 750 C in either H_2 or O_2 to produce clusters or atomic sites. The atomisation was found to be a deactivation mechanism when using the catalyst in oxidising environments, but this deactivation could be remedied not only by heating in H_2 but also by steam reforming the propene thus producing H_2.

Resume

Denne afhandling omhandler forskning inden for udvikling og karakterisering af termisk heterogene katalysatorer til brug under reaktionerne metanolsyntese fra CO_2, ætanolsyntese fra CO og propenoxidation til CO_2. De to første reaktioner er forslag til at syntetisere brændstoffer fra bæredygtig H_2 og opfanget CO_2, som enten bruges direkte eller reageret til CO først. Propenoxidation bruges som en modelreaktion til at undersøge katalysatorer med enkelt-atom-fikseret platin. I den præsenterede forskning er aktivitetseksperimenter for katalytisk aktivitet, elektronmikroskopi og spektroskopi, røntgendiffraktion og røntgenabsorption blevet brugt til at vurdere og karakterisere katalysatorerne.
Til metanolsyntesen fra CO_2 er en ternært legeret katalysator, Ni_2FeGa/SiO_2, blevet optimeret. Konklusion fra optimeringen var, at en temperatur på 550 C i H_2 under dannelsen af nanopartiklerne fra metalnitrater er optimal, når katalysatoren efterfølgende anvendes til metanolsyntese. Karakteriseringen belyste, at denne temperatur er optimal til dannelsen af legeringen, samtidig med at sintring undgåes. Ni_2FeGa/SiO_2 blev vurderet imod industriel $Cu/ZnO/Al_2O_3/MgO$, hvor de yder ens ved temperaturer under 200 C, dog har Ni_2FeGa/SiO_2 en laver selektivitet mod metanol.
Til ætanolsyntesen fra CO blev en ternært legeret katalysator, $CoCu_2Ga/SiO_2$, udtænkt og udviklet. Disse metaller er nøje udvalgt: kobolt og kobber, fordi litteraturen viser, at kombinationen af disse er en effektiv katalysator for ætanolsyntese; og gallium for at give legeringen stabilitet. Forskellige vægtconcentrationer af $CoCu_2Ga$ på SiO_2 blev syntetiseret og testet. En vægtconcentration på 3.5% $CoCu_2Ga$ producerede ætanol og i større mængder metanol og metan. Denne katalysator blev sammenlignet med indkøbt Rh/C, som for det meste lavede metan med mindre mængder ætanal, metanol og ætanol. Karakterisering viste, at ternære legerede nanopartikler faktisk blev dannet i $CoCu_2Ga/SiO_2$-katalysatorerne efter en syntese ved reduktion af metalnitrater ved 620 C i H_2. Ved en kombination af *in situ* røntgenmetoder og mikroskopi viste det sig, at små kobolt-rige partikler udskilles fra den ternære legering, når de opvarmes under reaktionsbetingelser.
Slutteligt blev en katalysator bestående af kun 0.05% vægtkoncentration platin supporteret på $MgAl_2O_4$ testet for propenoxidation. Denne katalysator viste sig at være meget katalytisk aktiv, når den bestod af små nano-klynger, og inaktiv, når platinet spreder sig til fikserede enkelt atomer. Disse tilstande viste sig at være reversible ved opvarmning over 750 C i enten H_2 eller O_2 for at producere nano-klynger eller atomariseret platin. Atomariseringen viste sig at være en deaktiveringsmekanisme, når katalysatoren blev brugt under oxiderende betingelser, men denne deaktivering kunne afhjælpes ikke kun ved opvarmning i H_2, men også ved dampreforming af propengassen som derved producerer H_2.

Acknowledgements

Two things I would like to point out, working as a PhD at Surfcat: it has been fun! And it has been a privilege! A privilege to interact on an everyday basis with the smartest and most inventive people. When wandering the halls and lunchroom of Surfcat and DTU Physics, you can not avoid finding people experienced and smart enough to solve what ever problem that you might bring. And researching in experimental physics certainly presents both opportunities and issues everyday.

The greatest privilege has been to interact with my supervisor Christian Danvad Damsgaard. He has been the greatest source of brilliance, who understood both the very practical issues I have encountered in the lab, as well as the grand scheme and where to go with our research. He has been a steadfast foundation under my work and the joy that I got out of researching. Christians guidance has carved the way for me to achieve my full potential in research and in life.
It goes without saying that I also owe immense gratitude to my co-supervisor Ib Chorkendorff. His grand knowledge, wide perspective and ability to immediately see when things look fishy, has been a catalyst for my learning through the years. There are oceans filled with things I would not understand, had he not supervised my research.
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A thanks go to my colleague and close friend Mads Lützen at DTU Nanolab, who towards the end of my PhD, helped me in conceiving significant parts of data and give me insight that I would not have gotten elsewhere.
Besides of all the researchers that I have collaborated with, a special thanks goes to my colleagues and the soul of Surfcat, the floor-managers Brian Knudsen, Jakob Ejler, and former floormanagers Patrick Strøm-Hansen and Kenneth Nielsen, as well as Jacqueline McAnulty and Birgit Bohn. My former office-mates through the PhD Jakob Pedersen, JP Haraldsted, Suzanne Zamany, Celia Cailloux and Sarah Shapel, I would like to thank, for making office-life enjoyable! Furthermore, I am thankful to Hjalte Armbjørner, Anton Lyksborg-Andersen and Mads Lützen (again), for their helpful spirit and insight in any kind of science. A blackboard always came in handy to conclude a discussion on fitting amplitudes in an absorption spectrum or on board-game statistics.

Deeply, I would like to thank my two partners in crime, Alexander Krabbe and Helene Hagemann, the PhD students who heat up the catalysis together with me. I cherish both the professional and the personal relationship that we have.
Finally my best character traits, my wife Anne and daughter Olivia. Olivia teaches me in a new way everyday, how to see the world. To Anne I owe all thanks, for the immense friendship and love I have gotten through all the years. It was her idea in the first place to study physics. I planned to be a historian (which might be the source of my verbose writing), or a pianist (though you will not find any rhythm in the text. Hopefully). But in the end those ideas never stuck. Initially I just tagged along with my wife, but quickly found out that physics is a field that I could use my

whole life on exploring.

Dedication

To conduct a PhD project is much like climbing a Mountain. To succeed is to reach the top. Stand in the lab and see that anomaly in the data that you hoped for. Or more often, did not expect. When you start the climb or start the PhD, you have an idea of, how it feels when you reach the top. But you have no idea, how it feels when you place your foot again on safe and sound ground at the bottom of the mountain. Finally writing this thesis has been a climb down the mountain for me, back to reality. Back to the perspective. Did I reach the top? Well, I could place the top anywhere I wanted. This thesis is not about the top. It is about the climb. I sincerely hope that whomever read these pages in the future, will find them useful and helpful for their own research. To all the PhD's that do not think they will ever reach the top: there are many horns to climb, and if you do not reach the top you have set, another will follow the path you have laid and come closer based on your work.

This thesis is dedicated to my wife, Anne. The brilliant hard working researcher that she is. And the loving person who is the source of what I call home. There is absolutely no way, I would have achieved my set goals in life without her. My personal character would simply not be the same, had we not found each other.

List of Publications Related to the Thesis

Paper 1, in appendix

Smitshuysen, T.E.L., Nielsen, M.R., Pruessmann, T., Zimina, A., Sheppard, T.L., Grunwaldt, J.-D., Chorkendorff, I., Damsgaard, C.D., Optimizing Ni-Fe-Ga alloys into Ni_2FeGa for the Hydrogenation of CO_2 into Methanol, *ChemCatChem*, **12**, 3265-3273 (2020), ref. [1]

Paper 2, in appendix

Chakraborty, D., Smitshuysen, T.E.L., Kakekhani, A., Fredsgaard, S.P., Banerjee, S., Hagen, N., Silva, H., Just, J., Damsgaard, C.D., Helveg, S., Rappe, A.M., Nørskov, J.K., Chorkendorff, I., Enhancing catalytic activity at ultra-low loading by reversible Pt atomization and nano-clustering on $MgAl_2O_4$ spinel, *in preparation*, 2022, ref. [2]

Paper 3,

Smitshuysen, T.E.L., Lützen, M., Zimina, A., Sheppard, T.L., Chorkendorff, I., Damsgaard, C.D., Addition of gallium in cobalt-copper alloys for the catalytic synthesis of ethanol, *in preparation*, 2022

Other publications related to the PhD project

Paper 4

Schumann, M., Nielsen, M.R., Smitshuysen, T.E.L., Hansen, T.W., Damsgaard, C.D., Yang, A.-C.A., Cargenllo, M., Grunwaldt, J.-D., Jensen, A.D., Christensen, J.M., Rationalizing an Unexpected Structure Sensitivity in Heterogeneous Catalysis-CO Hydrogenation over Rh as a Case Study, *ACS Catalysis*, **11**, 5189-5201 (2021), ref. [3]

Paper 5

Nielsen, N.D., Smitshuysen, T.E.L., Damsgaard, C.D., Jensen, A.D., Christensen, J.M., Characterization of oxide-supported Cu by infrared measurements on adsorbed CO, *Surface Science*, **703**, 121725 (2021), ref. [4]

Paper 6

Nielsen, M.R., Moss, A.B., Bjørnlund, A.S., Liu, X., Knop-Gericke, A., Klyushin, A.Y., Grunwaldt, J.-D., Sheppard, T.L., Doronkin, D.E., Zimina, A., Smitshuysen, T.E.L., Damsgaard, C.D., Wagner, J.B., Hansen, T.W., Reduction and carburization of iron oxides for Fischer–Tropsch Synthesis, *Journal of Energy Chemistry*, **51**, 48-61 (2020), ref. [5]

Paper 7

Eschenbacher, A., Saraeian, A., Jensen, P.A., Shanks, B.H., Li, C., Duus, J.Ø., Smitshuysen, T.E.L., Damsgaard, C.D., Hansen, A.B., Kling, K.I., Mentzel, U.V., Henriksen, U.B., Ahrenfeldt, J., Jensen, A.D., Deoxygenation of wheat straw fast pyrolysis vapors over Na-Al2O3 catalyst for production of bio-oil with low acidity, *Chemical Engineering Journal*, **394**, 124878 (2020), ref. [6]

Paper 8

Silva, H., Hernandez-Fernandez, P., Baden, A.K., Hellstern, H.L., Kovyakh, A., Wisaeus, E., Smitshuysen, T.E.L., Chorkendorff, I., Christensen, L.H., Chakraborty, D., Kallesøe, C., Supercritical flow synthesis of PtPdFe alloyed nanoparticles with enhanced low-temperature activity and thermal stability for propene oxidation under lean exhaust gas conditions, *Catalysis Science & Technology*, **9**, 6691-6699 (2019), ref. [7]

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Chapter 1

Introduction

This thesis presents research performed within heterogeneous thermal catalysis with emphasis on novel ternary alloys for the synthesis of methanol and ethanol, as well as more fundamental research into ultra-low loading noble catalysts. The intention of this first chapter is to give the reader an overview of, what heterogeneous thermal catalysis is and why it is an important field of research. It is not a technical prerequisite to read the first chapter, however for the layman an introduction is in order.

Our Way of Life Breathing down our Necks

Throughout human history, our standards of living have increased through our development of tools and ideas, that help us live and understand living. Inventions and engineering are improving our everyday life in such a pace and to such an extend that we cannot grasp the everyday-life predating modern technology or industrialisation, let alone having the least idea of what future generations might bring of technology. Such development do come at a cost. All the processes we use for manufacturing, transportation, entertainment, things that have been developed to solve problems and ease the way of life also requires input of energy. A good visualisation of this is shown in Figure 1.1 where the size of the gross domestic product(GDP) is shown versus the energy consumption for individual countries. The lines indicate the change from 2005 and to 2015. We see that poor countries move vertically up in energy-consumption where rich countries moves horizontally up in GDP. What seems to be the case is an activation-barrier of tens of MWh per person for getting over \$10k GDP[1] in order to achieve the way of life cherished in the developed world.

Beyond the activation-barrier in the developed world, the spread in both GDP and energy consumption is very large, which might stem from the different makeup of the respective industry of the specific country. If we look closely in Figure 1.1, some countries are actually moving down in energy consumption, exemplified by Denmark

[1] This is roughly the same size as the income-poverty line of the US.

Figure 1.1: Countries' annual energy consumption per capita versus their gross domestic product per capita shown as lines running from 2005 to 2015. Countries with less than 1 million inhabitants are omitted. GDP is in constant 2017 international $. Data is from https://ourworldindata.org/grapher/energy-use-per-capita-vs-gdp-per-capita .

in red bold font. The logic behind this behaviour is to be found on the back-side of the energy-consumption: the negative environmental impact.

The fact that parts of the world could develop into the high technology societies they are today, is carried by the use of fossil-fuels. Since the start of industrialisation and up to now, fossil-fuels such as oil, natural gas and coal used in combustion engines and manufacturing e.g., of plastic, inevitably end up in the end of the chemical food-chain as carbon dioxide. The left-axis on Figure 1.1 might as well have read CO_2-emission[2]. The emission of carbon dioxide and other green-house gasses have a huge impact on our climate by absorbing infrared radiation from the surface of the earth, thereby accelerating global warming leading to the rapid heating of our atmosphere observed in the last couple of decades.

The effect of this emission has so far contributed to an increase of about $1^{\circ}C$ in the global average temperature since the year 1900, shown in Figure 1.2(a). Of course a layman-argument could be that this is just coincidental and possible other factors are the cause. For the same reason, Figure 1.2(b) shows the predicted global temperature anomaly modelled by Broecker in 1975 based on predicted growth in fuel consumption and the available information at the time on, how global temperature respond to carbon dioxide-concentrations[9]. The resemblance between the temperature-curves in Figure 1.2(a) and (b) are remarkable and should make it quite clear that the

[2] The corresponding plot to Figure 1.1 is available at https://ourworldindata.org/grapher/co2-emissions-vs-gdp?xScale=linear&yScale=log .

(a) (b)

Figure 1.2: (a): Current data on global atmospheric CO_2 concentration and global change in temperature. Data-set from https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions , full details in [8]. (b): Modelled change to global temperature based on CO_2 emissions, natural climatic cycles, along with measurements from meteorological records. From Broecker (1975)[9]. Reprinted with permission from AAAS.

carbon dioxide turning the atmosphere into a greenhouse is an excellent explanation. The subsequent effects of rising global temperatures are felt today in the extreme weather and following events such as wild fires, droughts, floods, coral bleaching[10], not to mention the expected rising sea levels[11].

So in spite of the good things that fossil fuels have given us as a society, we cannot depend on them in the future, as the costs to the environment are far too high. Carbon-neutral energy sources are a bare necessity. But the challenge is not easy: currently the world consume 20 TW worth of energy, and with a large number of very populated countries still in need to develop, this consumption is bound to increase. So not only do we need to substitute all our current fossil-based sources; we need to meet the increasing demand as well. Nobel Laureate in chemistry (1996) Richard Smalley coined this challenge as the "Terawatt-challenge" in 2005[12]. The challenge to transition our energy system, but also to double the output. As Smalley formulated it, we need to find a "new oil". A "new oil" that can offer the same possibilities for prosperity in the coming centuries as fossil fuels have done in the past.

"New Oil" - Renewable Electricity

What could be the "New Oil"? Smalley puts his emphasis on renewable electricity with long-distance distribution and storage as a prerequisite[12]. He describes a solution based on solar-cells and nuclear powerplants with very small local storage-devices for electricity in every home able to run a household for a day[12]. Though[3]

[3] Smalley do not specify that the device is a battery, just that it is the size of a lectern. Maybe the point is to be open-minded.

Figure 1.3: The power-consumption and production from solar and wind on the Danish electrical grid during the year of 2021. Solar power is plotted on-top of wind power. The plot extends over two text-pages. An arrow indicate the same point in time on the di erent text-pages. Data from https://energinet.dk/Gron-omstilling/Noegletal-om-den-gronne-omstilling#vedvarende .

the political landscape has changed and the technologies have evolved in all kinds of direction since the ideas of Smalley,[4] renewable electricity is still the energy-source coming closest to the "new oil". In the following text, we will discuss current solutions with the Kingdom of Denmark as a case.

Case - Kingdom of Denmark

Renewable sources of electricity are highly based on what is available, eg. hydropower requires mountains and rivers, solar power requires sunshine. The Kingdom of Denmark is not blessed with any of these, but instead it has plenty of sea and wind. For the same reason, a very large portion of electricity in Denmark is produced by wind. Figure 1.3 shows the power-consumption in Denmark together with the power-output of Danish wind-turbines and solar-cells from Christmas of 2020 to Christmas of 2021. The demand has a very periodic and consistent pattern: during day and night time, the demand rises and falls with about 1.5 GW; day-dependent demand come in groups of ve high-demand days and two low-demand days being workdays and weekends; and the general power-demand increases during winter and decreases during summer. These behaviours make sense, as people has no need for power while they sleep, society use most power during the work-week, and at winter the houses need to be held warm and cosy. As for the renewable power production: it goes as the wind blows, maybe with a slight tendency to blow more during winter than summertime. There is a noticeable increase in solar power during the summer, though it is niche compared to wind power.[5] At few instances, the renewable electricity actually exceeds the demand. In total solar and wind produced the equivalent of 4% and 44% of the total power consumption since Christmas of

[4] Nuclear power-plants are not as popular as they could have been useful.

[5] But Denmark is also a very cold and dark country. Relatively speaking.