Hydrogen production from biomass wastes by reforming in hot compressed water

Studies with model oxygenates in the quest for finding an optimal catalyst

Anna Kaisa Kristiina Vikla
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<th>Name</th>
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</tbody>
</table>
Never give up.
Today is hard, tomorrow will be worse,
but day after tomorrow will be sunshine.
Jack Ma
# Table of Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Samenvatting</td>
<td></td>
<td>iv</td>
</tr>
<tr>
<td>Chapter 1</td>
<td>Objective and scope of this thesis</td>
<td>1</td>
</tr>
<tr>
<td>1.</td>
<td>Objective</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>Scope</td>
<td>4</td>
</tr>
<tr>
<td>3.</td>
<td>References</td>
<td>6</td>
</tr>
<tr>
<td>Chapter 2</td>
<td>Aqueous phase reforming of biomass based wastes</td>
<td>9</td>
</tr>
<tr>
<td>1.</td>
<td>Aqueous phase reforming (APR) definition</td>
<td>10</td>
</tr>
<tr>
<td>2.</td>
<td>Phase diagram - water</td>
<td>10</td>
</tr>
<tr>
<td>3.</td>
<td>Background - Hydrogen, steam reforming and water-gas shift</td>
<td>11</td>
</tr>
<tr>
<td>4.</td>
<td>Steam reforming/gasification of solid biomass</td>
<td>16</td>
</tr>
<tr>
<td>5.</td>
<td>APR of biomass streams</td>
<td>17</td>
</tr>
<tr>
<td>6.</td>
<td>References</td>
<td>36</td>
</tr>
<tr>
<td>Chapter 3</td>
<td>Experimental techniques</td>
<td>45</td>
</tr>
<tr>
<td>1.</td>
<td>Catalyst preparation</td>
<td>46</td>
</tr>
<tr>
<td>2.</td>
<td>Catalyst characterization</td>
<td>46</td>
</tr>
<tr>
<td>3.</td>
<td>Experimental setup for catalytic measurements</td>
<td>48</td>
</tr>
<tr>
<td>4.</td>
<td>Definitions</td>
<td>51</td>
</tr>
<tr>
<td>5.</td>
<td>References</td>
<td>54</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Towards stable catalysts for aqueous phase reforming of ethylene glycol for renewable hydrogen</td>
<td>59</td>
</tr>
<tr>
<td>1.</td>
<td>Introduction</td>
<td>60</td>
</tr>
<tr>
<td>2.</td>
<td>Experimental</td>
<td>61</td>
</tr>
<tr>
<td>3.</td>
<td>Results</td>
<td>63</td>
</tr>
<tr>
<td>4.</td>
<td>Discussion</td>
<td>67</td>
</tr>
<tr>
<td>5.</td>
<td>Conclusions</td>
<td>69</td>
</tr>
<tr>
<td>6.</td>
<td>References</td>
<td>69</td>
</tr>
</tbody>
</table>
# Chapter 5

Development of stable catalyst supports for aqueous phase reforming of oxygenates – Studies with hydroxyacetone

1. Introduction 74  
2. Experimental 75  
3. Results 77  
4. Discussion 86  
5. Conclusions 97  
6. References

# Chapter 6

Tuning the characteristics of Pt/C catalysts for aqueous phase reforming of biomass related oxygenates 107

1. Introduction 109  
2. Experimental 110  
3. Results 113  
4. Discussion 125  
5. Conclusions 130  
6. References 130

# Chapter 7

Investigation of diffusional effects in aqueous phase reforming of hydroxyacetone over Pt/C catalysts 133

1. Introduction 134  
2. Experimental 136  
3. Results 137  
4. Discussion 147  
5. Conclusions 152  
6. References 152

# Chapter 8

Conclusions and further suggestions 157

1. Conclusions 158  
2. Remarks for future research based on the findings in this thesis 159

Acknowledgements 161

Scientific contributions 166
Summary

For the past three decades increasing concerns for climate pollution and depletion of fossil fuel sources have driven scientists to seek for alternative, sustainable sources of energy. Today, the concerns are higher than ever and solutions are not just scientifically challenged, but also politically and morally challenged. It is paramount that societies switch to more sustainable usage of energy and other resources to decrease their impact on the environment in the coming years. The quest for renewable energy production is still ongoing and it is crucial to find ways to produce them feasibly in order to provide replacement for fossil energy sources.

Biomass is a promising renewable source and it can partly provide for the need of sustainable energy. There are multiple ways to convert biomass to energy. For production of liquid fuels, e.g. for transportation sector, pyrolysis is the most promising option. In this process the biomass based solid feedstock is converted at a high temperature (> 300 °C) in an inert atmosphere in a matter of seconds to a liquid. Due to the nature of biomass, this liquid contains components that form an oil phase and a water-based phase, an aqueous phase. The oil phase as such is not stable and it needs to be upgraded to be used as conventional oil and it needs hydrogen. Hydrogen at the moment is mainly produced by fossil sources. However, the aqueous phase that is left from pyrolysis contains organic molecules, such as sugars, acids, alcohols, ketones, that can be converted to hydrogen and carbon dioxide. As water content of this phase is high, utilization of these molecules for steam reforming/gasification by evaporation of the water would be energy intensive. Aqueous phase reforming (APR) has been developed to process these types of diluted streams to hydrogen while keeping the water in liquid phase. APR is typically operated at 200-275 °C, at elevated pressures and a catalyst is required for efficient conversion of the feedstock to hydrogen. It has been shown earlier that design of stable and active catalyst for this process is challenging due to the drastic conditions used in APR. However, this step has to be overcome for commercialization of APR. In this thesis development of stable and active catalyst for APR is studied.

In Chapter 1 the objective and scope for this study is elaborated. The challenges for commercialization of APR in terms of catalyst development are discussed. These facts are used to set the scope for the research described in the later chapters.

Background for APR is explained in Chapter 2 with the current status. Catalytical hydrogen production from biomass based wastes is discussed in detail.

In Chapter 3 the experimental techniques are explained. Techniques for catalyst preparation is briefly discussed along with characterization techniques used to determine the properties of the materials studied in APR. The setup for APR studies is also described along the methods used for determining product distributions.

Important quality for a catalyst is its stability under the conditions studied. Due to drastic APR conditions some catalyst supports suffer from phase transformation. In Chapter 4, we prepared a Platinum catalyst on a support (AlO(OH), boehmite) that had
already gone through phase transformation from γ-alumina. The performance of this catalyst was then compared to Pt/γ-Al2O3, a catalyst initially active in APR. Under APR of 5wt% of ethylene glycol (EG) at 270 °C/90 bar Pt/AlO(OH) showed stable performance and surprisingly, a higher hydrogen formation rate than Pt/Al2O3 which deactivated due to phase change of the support. The higher hydrogen rate of Pt/AlO(OH) was suggested to be due to its hydroxylated form that enhances reforming of carbonaceous species on the catalysts surface or due to enhanced oxidation of Pt. Due to the stability and selectivity to hydrogen Pt/AlO(OH) shows great promise as an APR catalyst.

In Chapter 5 the APR studies are continued with a more challenging model component, hydroxyacetone (HYDA). HYDA is a major ketone component in aqueous phase of pyrolysis oil. Three catalysts were prepared on supports known to be hydrothermally stable, Pt/AlO(OH), Pt/ZrO2 and Pt/C. The catalysts were studied in APR of 2.5wt% HYDA under 225 °C/35 bar. All the catalysts showed initially high activity for HYDA conversion, however, the oxide supported catalyst deactivated rapidly due to formation of coke on the catalysts caused by liquid phase conversion of the feed. Pt/C catalyst remained stable and active during time on stream. The catalyst converted most of the feed to gas phase products and preventing formation of liquid by-products that could lead formation of coke/char. The gas phase products were mostly H2, CO, CO2 and CH4. The stability of the carbon support and its resilience towards coking showed promise for further study in APR. In addition, carbon supported catalysts can be easier handled after use as the carbon can be burned and metal harvested for recycling. This set a good starting point for a further development for APR application.

In APR activity and selectivity of the catalyst for hydrogen is essential for feasible operation. Selectivity can be altered by changing the properties of the catalyst or by changing the reaction conditions. In Chapter 6 we studied further Pt/C catalyst, by preparing them by different methods in order to alter the particle size of Pt and its distribution on the carbon support. Catalysts named as Pt-IM, Pt-OX, Pt-PR and Pt-CL, were characterized with multiple methods to learn in detail the metal size and distribution. Transmission electron microscopy (TEM) was applied with X-ray photoelectron spectroscopy to view the cross-sections of the catalysts grains. These confirmed that Pt-PR and Pt-CL had more of an egg-shell type structure compared to Pt-IM and Pt-OX which had more uniform distribution of Pt on the carbon supports. The catalysts were tested in APR of 2.5wt% of EG at 225 °C and 35 bar. All catalysts were stable under these conditions during 420 minutes on stream. The results showed that the egg-shell type structure was more favorable for hydrogen turnover rate. Further, larger Pt particles seemed to enhance C-C bond cleavage and improve hydrogen production. Findings support that Pt/C is an good choice for a catalysts in APR.

In Chapter 7 effect of mass transfer and reaction temperature for product selectivity was studied for APR of HYDA over Pt/C catalysts. Two types of mass transfer can influence the catalysts performance, 1) external mass transfer that lowers the conversion rate and 2) internal mass transfer that affects the product selectivity. For this study catalysts were prepared 1.4wt% Pt/C with grain size of 100-250 µm, named as I-Pt/C and 1.7wt% Pt/C with grain size of 70-100 µm, named as II-Pt/C. Stability of these catalysts were studied at 2.5wt% of HYDA at 225 °C/35 bar to confirm that stability was not an issue for the rest of
the study. External mass transfer was studied for both catalysts by keeping ratio of catalyst weight and feed flowrate similar and internal mass transfer was studied by comparing product selectivities under the studied conditions between I-Pt/C (100-250 μm) and II-Pt/C (70-100 μm). Results in comparison with transport criteria showed that external mass transfer was not an issue in our studied conditions. Internal mass transfer could not be explicitly ruled out by the results, however, the calculated transport criteria showed that it is unlikely. The effect of reaction temperature on product selectivity was also measured at 250 °C/50 bar and attempts were made to calculate activation energy. Unfortunately, almost full conversion was obtained at 250 °C and therefore it was not possible to calculate activation energy with this test data. Increase in temperature from 225 °C to 250 °C did improve Water-Gas Shift (WGS) reaction and therefore hydrogen selectivity. This confirms that Pt/C has potential to be developed for APR.

In Chapter 8 the work in this thesis is concluded and remarks for further research are given. This thesis focused on finding a stable and active catalyst for APR of biomass based feedstocks. The studied Pt/C catalyst was highly promising due to its stable mesoporous structure and activity towards gas phase products to prevent coking. The usage of carbon as a support material also enables to recycle the metal after use, which will add to more sustainable process. Further development of Pt/C catalysts should be focused to improve the WGS activity of the catalyst and to study the ways to prevent methane formation in order to take steps closer for commercialization of APR application.
Samenvatting

De afgelopen drie decennia heeft de ongerustheid rondom klimaatvervuiling en het uitputten van fossiele brandstoffen wetenschappers gedreven om alternatieve, duurzame energiebronnen te zoeken. Vandaag de dag is de ongerustheid hoger dan ooit en de oplossingen zijn niet alleen wetenschappelijk gezien uitdagend, maar ook politiek en moreel gezien. Het is van het grootste belang dat samenlevingen omschakelen naar het gebruik van duurzame energie en andere grondstoffen om hun impact op het milieu af te laten nemen. De zoektocht naar duurzame energieproductie is nog steeds aan de gang en het is cruciaal om manieren te vinden om ze op een haalbare manier te produceren om fossiele brandstoffen te kunnen vervangen.

Biomassa is een veelbelovende hernieuwbare bron en kan deels voorzien in de behoefte van duurzame energie. Er zijn meerdere manieren om biomassa om te zetten in energie. Voor de productie van vloeibare brandstoffen, bijv. voor de transportsector, is pyrolyse de meest belovende optie. In dit proces wordt de op biomassa gebaseerde vaste grondstof in enkele seconden op hoge temperatuur (> 500 °C) omgezet in een vloeistof. Vanwege de aard van biomassa bevat deze vloeistof componenten die een oliefase en een fase op waterbasis vormen, een waterige fase. De oliefase is als zodanig niet stabiel en moet worden opgewaardeerd om gebruikt te worden als conventionele olie en het heeft waterstof nodig. Waterstof wordt op dit moment voornamelijk geproduceerd met fossiele bronnen. De waterige fase die overblijft na pyrolyse bevat echter organische moleculen, zoals suikers, zuren, alcoholen, ketonen, die omgezet kunnen worden in waterstof en koolstofdioxide. Aangezien het watergehalte van deze fase hoog is, zou het gebruik van deze moleculen voor stoomreforming/vergassing door verdamping van het water energie-intensief zijn. Waterige fase reforming (APR, Aqueous Phase Reforming) is ontwikkeld om dit soort verdure stromen te verwerken tot waterstof, terwijl het water in vloeibare fase blijft. APR wordt doorgaans uitgevoerd bij 200–275 °C onder verhoogde druk en een katalysator is vereist voor een efficiënte omzetting van de grondstof in waterstof. Het is eerder al aangetoond dat het ontwerpen van stabiele en actieve katalysatoren voor dit proces een uitdaging is, vanwege de drastische omstandigheden die in APR worden gebruikt. Deze stap moet echter overwonnen worden voor de commercialisering van APR. In dit proefschrift wordt de ontwikkeling van stabiele en actieve katalysatoren voor APR bestudeerd.

In hoofdstuk 1 wordt het doel en bereik van deze studie uitgewerkt. De uitdagingen voor de commercialisering van APR worden besproken in termen van katalysatorontwikkeling. Deze feiten worden gebruikt om het bereik voor het onderzoek te bepalen dat in de latere hoofdstukken wordt beschreven.

De achtergrond voor APR wordt uitgelegd in hoofdstuk 2 met de huidige status. De productie van katalytische waterstof uit afvalstoffen van biomassa wordt in detail besproken.

In hoofdstuk 3 worden de experimentele technieken uitgelegd. Technieken voor katalysatorbereiding worden kort besproken naast de karakterisatietechnieken, welke
gebruikt worden om de eigenschappen van de in APR onderzochte materialen te bepalen. De opstelling voor APR-onderzoeken wordt ook beschreven volgens de methoden die worden gebruikt voor het bepalen van productverdelingen.

Een belangrijke kwaliteit voor een katalysator is zijn stabiliteit onder de bestudeerde omstandigheden. Vanwege de drastische APR-omstandigheden lijden sommige katalysatordragers aan fasetransformatie. In Hoofdstuk 4 hebben we een platina-katalysator bereid op een drager (AlO(OH), boehmite) die al door fasetransformatie van γ-alumina was gegaan. De prestatie van deze katalysator werd vervolgens vergeleken met Pt/γ-Al₂O₃, een katalysator die aanvankelijk actief was in APR. Onder APR van 5 gew.% ethyleenglycol (EG) bij 270 °C / 90 bar bleek Pt/AlO(OH) een stabiele prestatie en verrassenderwijs een hogere waterstofvormingssnelheid dan Pt/Al₂O₃, die werd gedeactiveerd als gevolg van faseverandering van de drager. De hogere waterstofsnellheid van Pt/AlO(OH) werd gesuggereerd als gevolg van zijn gehydroxyleerde vorm, die het reformen van koolstofhoudende soorten op het oppervlak van de katalysator, of door verbeterde oxidatie van Pt. Vanwege de stabiliteit en selectiviteit voor waterstof is Pt/AlO(OH) veelbelovend als een APR-katalysator.

In Hoofdstuk 5 worden de APR-onderzoeken voortgezet met een uitdagend modelcomponent, hydroxyacetone (HYDA). HYDA is een belangrijke ketoncomponent in waterige fase van pyrolyseolie. Drie katalysatoren zijn bereid op dragers waarvan bekend is dat ze hydrothermisch stabiel zijn, Pt/AlO(OH), Pt/ZrO₂ en Pt/C. De katalysatoren zijn bestudeerd in APR van 25 gew.% HYDA onder 225 °C / 35 bar. Alle katalysatoren vertoonden aanvankelijk een hoge activiteit voor HYDA-omzetting, maar de op okside gedragen katalysator deactiveerde snel vanwege de vorming van coke op de katalysatoren, veroorzaakt door de omzetting in vloeibare fase van de grondstof. Pt/C-katalysator bleef gedurende het experiment stabiel en actief. De katalysator converteerde het merendeel van de grondstof naar gasfaseproducten en voorkwam vorming van vloeibare bijproducten die tot de vorming van coke/koolstof zouden kunnen leiden. De gasfaseproducten waren meestal H₂, CO, CO₂ en CH₄. De stabilité van de koolstofdrager en zijn veerkrachtige aanzien van coke-vorming zijn veelbelovend voor verder onderzoek in APR. Bovendien kunnen katalysatoren op koolstofdragers na het gebruik makkelijker verwerkt worden omdat de koolstofverbranding kan worden en metaal kan worden geoogst voor recycling. Dit vormt een goed startpunt voor een verdere ontwikkeling voor de APR-toepassing.

In APR is de activiteit en selectiviteit van de katalysator voor waterstof essentieel voor een haalbare werking. Selectiviteit kan worden veranderd door de eigenschappen van de katalysator te veranderen of door de reactieomstandigheden te veranderen. In Hoofdstuk 6 hebben we de Pt/C-katalysator verder bestudeerd, door deze op verschillende manieren te bereiden om de deeltjesgrootte van Pt en de verdeling ervan op de koolstofdrager te veranderen. Katalysatoren genoemd als Pt-IM, Pt-OX, Pt-PR en Pt-CL, werden gekenmerkt met meerdere methoden om in detail de metaafmeting en -verdeling te leren. Transmissie-elektronenmicroscopie (TEM) werd aangebracht met röntgenfoto-elektronenspectroscoopie om de dwarsdoorsnede van de katalysatorkorrels te bekijken. Deze bevestigden dat Pt-PR en Pt-CL meer een structuur van het eischaal-type hadden vergeleken met Pt-IM en Pt-OX, die meer uniforme platina-verdeling hadden. De
Samenvatting

Katalysatoren werden getest in APR van 2,5 gew.% EG bij 225 °C en 35 bar. Alle katalysatoren waren stabiel onder deze omstandigheden gedurende 420 minuten in de stroom. De resultaten toonden aan dat de structuur van het eischaal-type gunstiger was voor de snelheid van waterstofomzetting. Verder leken grotere Pt-deeltjes de C-C-bindingsplitsing te verbeteren en de waterstofproductie te verbeteren. Deze bevindingen ondersteunen dat Pt/C een goede keuze is voor katalysatoren in APR.

In Hoofdstuk 7 werd het effect van massaoverdracht en reactietemperatuur voor productselectiviteit bestudeerd voor APR van HYDA op Pt/C-katalysatoren. Twee soorten massaoverdracht kunnen de prestaties van de katalysator beïnvloeden, 1) externe massaoverdracht die de conversiesnelheid verlaagt en 2) interne massaoverdracht die de conversiesnelheid en de productselectiviteit beïnvloedt. Voor dit onderzoek werden 2 katalysatoren bereid met 1,4 gew.% Pt/C met een korrelgrootte van 100-250 μm, genoemd als I-Pt/C en 1,7 gew.% Pt/C met een korrelgrootte van 70-100 μm, genoemd als II-Pt/C. De stabilititeit van deze katalysatoren werd bestudeerd bij 2,5 gew.% HYDA bij 225 °C / 35 bar om te bevestigen dat de stabiliteit geen probleem was voor de rest van het onderzoek. Externe massaoverdracht werd bestudeerd voor beide katalysatoren door de verhouding van katalysatorgewicht en grondstof stroomsnelheid gelijk te houden en interne massaoverdracht werd bestudeerd door productselectiviteit te vergelijken onder de bestudeerde omstandigheden tussen I-Pt/C (100-250 μm) en II-Pt/C (70-100 μm). Resultaten in vergelijking met transportcriteria toonden aan dat externe massaoverdracht geen probleem was onder onze bestudeerde omstandigheden. Interne massaoverdracht kon niet expliciet worden uitgesloten door de resultaten, maar de berekende transportcriteria toonden aan dat het onwaarschijnlijk is. Het effect van de reactietemperatuur voor productselectiviteit werd ook gemeten bij 250 °C / 50 bar en pogingen werden gedaan om de activeringsenergie te berekenen. Helaas werd bijna volledige conversie verkregen bij 250 °C en daarom was het niet mogelijk om activeringsenergie te berekenen met deze testgevens. Verhoging van de temperatuur van 225 °C tot 250 °C verbeterde de Water-Gas-Shift (WGS) reactie en dus de waterstof selectiviteit. Dit bevestigt dat Pt/C potentieel heeft om te worden ontwikkeld voor APR.

In hoofdstuk 8 wordt het werk in dit proefschrift afgerond en worden aanbevelingen gegeven voor verder onderzoek. Dit proefschrift richtte zich op het vinden van een stabiele en actieve katalysator voor APR van op biomassagebaseerde grondstoffen. De bestudeerde Pt/C-katalysator was veelbelovend vanwege de stabiele mesoporeuze structuur en activiteit ten opzichte van gasfaseproducten om coke-vorming te voorkomen. Het gebruik van koolstof als dragermateriaal maakt het ook mogelijk om het metaal na gebruik te recyclen, wat zal bijdragen aan een duurzamer proces. Verdere ontwikkeling van Pt/C-katalysatoren moet gericht zijn op het verbeteren van de WGS-activiteit van de katalysator en het bestuderen van manieren om methaanvorming te voorkomen om volgende stappen te zetten voor de commercialisering van APR-toepassing.
Chapter 1

Objective and scope of this thesis

Aqueous phase reforming is a promising technology for more sustainable hydrogen production. In this chapter the objective for the research is discussed taking into account the challenges that further development of this technology is facing. The chapter is finished with the scope for the work in this thesis.
1 Objective

Waste water streams from e.g. food industries or bio-refineries have aqueous effluents that contain dissolved organics, usually in the range of 5-20 wt%. One typical example is the aqueous phase of pyrolysis oil which contains variety of oxygenates such as acids, aldehydes, ketones, alcohols, sugars to name a few [1, 2]. For processing these chemicals to hydrogen, Dumesic and co-workers first introduced “Aqueous Phase Reforming” (APR) [2]. The concept was further demonstrated for water reforming of diluted oxygenate feeds at mild temperatures in pressurized liquid water (225 – 265 °C, 29 – 56 bar) over supported metal catalysts [3-5]. For example, typical temperatures for fundamental APR studies of model components (e.g. ethylene glycol, methanol and sorbitol) were usually performed in the temperature range of 200-265 °C [6, 7]. The purpose of these studies has been to identify pathways that lead to hydrogen and prevent formation of by-products.

The reaction rates are slower at the above-mentioned temperatures and therefore studies are limited to feed solutions of low concentrations or long residence times. The ultimate goal should be to develop a commercially and technologically feasible (catalytic) process for the production of hydrogen by APR of industrial biomass derived aqueous streams that contain complex mixtures (15–25 wt%) of oxygenates. Therefore, much higher reaction rates are required compared to low temperature APR to achieve this goal. Achieving high H\textsubscript{2} yields by reforming of highly concentrated feeds is not just a matter of increasing the catalytic efficiency. Thermodynamics predict an increase in alkane formation for reforming reactions with higher feed concentrations [4]. Production of alkanes should be avoided as it competes with the hydrogen yields. Furthermore, low temperature APR is also reported to be subject to mass transfer limitations, which can severely hinder the catalytic reaction for high feed concentrations. As an example, it was shown by Shabaker and colleagues [6] that APR of ethylene glycol (225°C and 29.3 bar) with a 3.4 wt% Pt/Al\textsubscript{2}O\textsubscript{3} (63–125 mm particle size) catalyst was affected by intra-particle mass transfer limitations when an ethylene glycol feed concentration of 10 wt% was used. Interestingly, catalytic supercritical water reforming is promising for achieving high reforming rates and overcoming mass transfer limitations. Supercritical water provides a medium with better heat transfer than is commonly in the gas phase and a higher diffusivity than in the liquid phase [8, 9]. Guo et al. [8] published an excellent overview of catalytic supercritical water reforming studies of biomass derived compounds. High reaction rates for the reforming of concentrated oxygenated hydrocarbon streams were reported. However, supercritical water reforming is energy intensive and due to the harsh conditions used materials, catalysts and reactor setups often worn out quickly. The temperature that are more of interests for APR studies are in the subcritical range (200-300 °C). Feeds for APR are oxygenated hydrocarbons that are also more reactive than typical steam reforming (SR) hydrocarbons, e.g. methane. Due to this advantage, it is promising to study APR in the subcritical water conditions. In general, stability and hydrogen selectivity issues
with the studied catalysts are serious drawbacks for industrial exploitation of this process [8].

Catalyst stability issues in hot compressed water are mainly related to sintering of the supported metal particles [8] or instability of conventional metal oxide catalyst supports (e.g. \(\text{Al}_2\text{O}_3, \text{TiO}_2, \text{ZrO}_2\)) [10, 11]. Issues with metal oxide supports, e.g. hydration/dehydration and phase transformation are already experienced at low temperature APR conditions [12]. Several authors have discussed the hydrothermal stability of catalysts in APR of model feedstocks [13-16]. Higher polyol feeds can enhance the stability of alumina against dehydration, however, under acid feeds the support suffers from severe deactivation.

In addition to support instability, the stability of supported catalytic metal components are also a critical issue. Commonly used steam reforming catalysts are Ni based as they are very active and cheap for commercial application. Water-Gas Shift reaction (WGS) that is needed to maximize hydrogen yields after SR, uses Ni and Cu metals in separate stages. However, solubility/leaching of such metals in high temperature and pressurized water is a real problem. Cu is also very sensitive to oxidation/poisoning, both of which lead to rapid deactivation, by oxygenates, char. Pt is a possible single stage WGS reaction as it overcomes problems related to both Ni, and Cu discussed above [5, 7, 17].

Furthermore, catalyst deactivation due to coke and char formation is still a major issue in the successful design of efficient catalysts. A variety of reports have addressed the issue of coke/char formation during APR of oxygenated feedstocks [16, 18, 19]. Acetic acid is often studied, as it is one of the most problem components during steam reforming with regards to coke formation [20-24]. Acetic acid is also one of the products observed in significant amounts during APR conversion of most oxygenates due to oxidation of the feed molecule by water [14, 16, 25-27]. Acetic acid easily undergoes ketonization/aldol condensation to form coke forming precursors, such as acetone, diacetone alcohol and ketene. Thus, coke formation on the catalysts is a real issue. For commercial application coke regeneration is an option, however, a reasonable period of stable activity (no rapid deactivation) is essential.

Key to designing an efficient catalyst relies on understanding the (1) chemical and physical properties of the oxide support and active metal component and (2) reaction chemistry involving the route to the formation of side products that affect hydrogen yields and formation of the precursors to coke/char formation. The key challenge for chemistry and catalyst during APR is to achieve C-C bond cleavage, to result in C1 specie which on further oxidation by water yields carbon oxides (\(\text{CO}, \text{CO}_2\)) and hydrogen. In terms of products, complete conversion of feed/reactant oxygenates to \(\text{CO}_2\) and maximize hydrogen yields is essential. For oxygenated hydrocarbons with C/O ratio of 1 the Equations 1-3 shows the stoichiometry of the reactions. WGS reaction is shown in Eq. 2.
\[ C_xH_{2x}O_x \leftrightarrow xCO + xH_2 \]  \hspace{1cm} (1)

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]  \hspace{1cm} (2)

\[ C_xH_{2x}O_x + xH_2O \leftrightarrow xCO_2 + 2xH_2 \]  \hspace{1cm} (3)

Formation of alkanes, especially methane which is thermodynamically favourable under APR conditions, lower hydrogen yields and should be minimized. Further, also liquid products, such as acids, aldehydes, alcohols etc., when formed remain in the aqueous phase and cause incomplete conversion of the feed reactant. Some of these products are unstable and via secondary reactions, such as condensation, polymerization, form coke/char/tar and destabilize catalysts.

To summarize, the challenge to make sub- or supercritical water reforming of biomass derived waste streams requires design of catalysts that (i) show high stability in hot compressed water and are stable against impurities or poisons, such as tars, (ii) minimize coke/char formation, (iii) are able to convert high concentrated feed streams under industrially relevant residence times, i.e, have high catalytic activity, and (iv) maximize H\textsubscript{2} yields.

## 2 Scope for this thesis

The main goal of this thesis is to understand issues that affect catalyst stability and effect of catalyst properties for maximized hydrogen yields using model feedstock molecules. Furthermore, understanding formation of side products and they role in deactivation/stability of the catalyst is essential. With this in mind, APR studies are conducted with low feed concentrations 2.5-5wt\% of reactant and at temperature range of 225-270 °C under 35-90 bar. The premise is that: (i) under these conditions reaction rates are relatively high to study catalyst performance. (ii) Furthermore, mass transfer limitations are minimized. At higher temperature and pressure, rates would get higher and solubility of coke and tars would increase, but also due these properties not only catalyst materials are challenged, but also the materials for the reactor setup. (iii) Lower temperature would only slower reaction rates and are typically more beneficial for FT (Fischer-Tropsch) and hydrogenation.

Chapter 2 will present the background hydrogen production from conventional methods and via sustainable biomass sources. Thermodynamics, the benefits of APR and chemistry under these conditions among the current challenges are also discussed. This chapter is adapted from the following publication:

Objective and scope

Experimental techniques used for catalyst characterization are explained in detail in Chapter 3. This chapter also presents the evaluation criteria for catalyst performance among the equipment and techniques for the APR studies carried out in this thesis.

Addressing catalyst stability is the first challenge for this study. In literature, a well-known steam reforming catalyst Pt/γ-Al₂O₃ has been reported to deactivate rapidly during APR of Ethylene Glycol (EG). Deactivation is caused by phase change of the support to hydrated form of alumina, AIO(OH). In Chapter 4, we compare stability and activity of Pt supported on γ-Al₂O₃ and the already hydrated form, AIO(OH). The reforming studies are carried out in subcritical APR conditions using EG as a model compound. Our results show that surprisingly the Pt/AIO(OH) catalyst is found to be stable, but also having a higher H₂ formation rate per Pt surface atom than Pt/γ-Al₂O₃. This chapter was published as a following publication:


Biomass feeds are complex solutions of molecules with different functionalities. Many studies in APR are focusing on EG as model compound due to its presence in bio feedstocks, but also due to its simple structure. Having only one C-C bond with both carbons connected to OH-groups enables one to study the preferred routes of the used catalyst, such as dehydrogenation or C-C bond reactions. However, a catalyst stable and active for EG reforming can be challenged when subjected to more complex feeds. In Chapter 5, APR of one of the most abundant ketone component in biomass solutions, hydroxy-acetone (HYDA) is studied over three different catalysts. The catalysts are Pt supported on hydrothermally stable materials, AIO(OH), ZrO₂ and Carbon. The results are discussed by looking into detail the products formed and how they are related to the properties of the catalysts. This is then linked to the catalyst stability and selectivity to hydrogen.


In Chapter 6 a more in-depth view in the properties of carbon supported APR catalysts is taken. Catalysts with different properties are prepared and tested in APR of EG. More detailed characterizations are performed to understand the performance of the studied catalysts. In the light of this knowledge more insight is gained how how the catalyst properties affect APR performance.

Mass transfer challenges in APR are discussed in Chapter 7. Factors affecting external mass transfer and internal mass transfer are investigated for Pt/C catalysts. The findings underline the importance of factors, such as catalyst grain size and chosen conditions.


In Chapter 8 highlights the conclusions of this work and also gives suggestions for the future development of APR catalysts. The thesis is completed with acknowledgements for this work.

3 References

Chapter 2

Aqueous phase reforming of biomass based wastes

Global energy demand and environmental concerns are driving factors for sustainable fuel production. Aqueous phase reforming is a technology that can provide a way to reduce wastes from bio-oil industry and food industries. In Chapter 2, the current status and issues involved in the production of hydrogen via catalytic aqueous phase reforming of biomass based waste streams is discussed.

1 Aqueous Phase Reforming (APR) definition

Steam reforming reaction uses water as oxidant to generate syngas (CO + H₂) from hydrocarbons, e.g., methane. This strongly endothermic reaction is carried out at high temperatures (>750 °C) and low pressures (< 25 bar) where water is in the gas phase. Aqueous phase reforming is a variant where conditions are maintained to keep water in the liquid phase. The feedstock in this case is an aqueous phase containing dissolved organics, typically in the range of 5-20 wt%. The reaction equation for carbohydrates, waste from a food industry, for example, is,

\[ C_6H_{12}O_6 + 6 H_2O \rightarrow 6 CO_2 + 12H_2 \]  

(1)

The conversion of such aqueous bio/organic wastes (>80% water) into high value products such as hydrogen, syngas (CO/H₂) using conventional reforming processes which operate at lower pressures and high temperatures is energy intensive due to also the need to account for the latent heat of evaporation of water. DuMeSoic and co-workers tackled this problem by developing the “Aqueous Phase Reforming” (APR) process in which water is kept in the liquid phase by applying elevated pressures [4-6]. The concept was further demonstrated for steam reforming of diluted oxygenate feeds at mild temperatures in pressurized liquid water (225–265 °C, 29–56 bar) over supported metal catalysts. For example, typical temperatures for fundamental APR studies of model components (e.g. ethylene glycol, methanol and sorbitol) are usually performed in the temperature range of 200-265 °C [5, 7]. The reforming of higher concentrated feed streams or more complex oxygenated hydrocarbons, which are of more commercial relevance, require higher temperatures to obtain the reaction rates which are necessary for industrial application [8].

Generation of chemicals from renewable bio-based feedstocks often involve a hydrogenation step. In order to make these conversions completely green it is essential that the required hydrogen for this is also made available from bio feedstocks. This chapter addresses the issues involved in the production of hydrogen via APR of byproduct waste streams. APR has also been used sparingly, to refer to reactions occurring in aqueous phase to generate valuable aromatic molecules, e.g. from lignin via depolymerisation. Hydrogen generated in the presence of catalysts under higher pressures and temperatures facilitate this reaction and hence the use of the term APR. This will be discussed later in the chapter.

2 Phase diagram – water

The phase diagram of water given in Figure 1 shows the pressures required to keep hot water in the liquid phase at elevated temperatures. APR conditions can thus be divided into sub- and supercritical regimes. The transition from sub- to supercritical water occurs at 374 °C and 221 bar. A dramatic change in the properties of water occurs
when water becomes supercritical and these offer some advantages for the reforming of biomass derived waste streams into gaseous products [8-11]. The density beyond the supercritical point is around ± 100 kg/m³ and further increase in temperature does not affect the density significantly anymore. The properties of liquid water and compressed gas converge around the supercritical point, resulting in complete mixture of both phases and the removal of the liquid/gas phase boundary. The latter is very beneficial for fast rates of heat and mass transfer [8], the latter being very relevant for bulky organic molecules.

Justifiably, APR is also termed “Gasification in Hot Compressed Water”, which includes also supercritical conditions where water is not a liquid and where feed molecules in liquid or solid phase are converted into gases.

3 Background – Hydrogen, steam reforming and water gas shift

3.1 Current status

Currently, syngas is mostly produced by steam reforming of natural gas and other fossil feedstocks. Hydrogen yields are maximised by a subsequent water gas shift reaction, discussed later. Around 60 million tons of hydrogen is produced globally in 2017 [12] and the demand for it is ever increasing. In Europe it is predicted that yearly
growth 3.5% (estimated in 2015, see Figure 2) [13]. Currently, hydrogen is widely used in ammonia production for fertilizer industry, oil refining and food industry.

Steam reforming of natural gas is the most a proven and used technology for the production of hydrogen [14-16]. The first industrial steam reformer was installed as early as 1930 [16]. Most of the commercial activities were in the United States where natural gas was abundantly available. Later on, discovery of natural gas reserves in Europe allowed use natural gas as feedstock for hydrogen production. Steam reforming is a strongly endothermic reaction (Eq. 2). In order to ensure a high methane conversion it is therefore required to operate at elevated temperatures.

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad (\Delta H \approx 206.3 \text{ kJ/mol}) \quad (2)$$

Additionally, steam reforming reaction is reversible. Therefore, according to Le Chatelier’s principle, low pressures and relatively high steam to carbon ratios will shift the equilibrium to the right increasing methane conversion, as illustrated in Figure 3 [15, 17]. Methane, particularly, is extremely difficult to activate, as the hydrogen-carbon bonds [9] are strong (435 kJ.mol$^{-1}$) and therefore cleavage of the corresponding hydrogen-carbon bonds requires very high temperatures. The presence of a catalyst, however, allows for milder conditions as it enhances the hydrogen carbon bond rupture. The metals of group VIII of the periodic table are active for steam reforming and particularly Ni appears to be the most cost-effective [16, 17].

![Figure 2. Hydrogen demand and estimation to year 2025 in Europe. Dashed lines indicate the yearly predicted increase. After Fraille et al. [13]](image-url)
Industry typically operates this process at around 800 °C, 15-40 bar and a steam to carbon ratios of 2-3 over Ni based catalysts [18, 19]. Although the presence of a catalyst makes the process technically more feasible as compared to non-catalytic conditions, the elevated temperatures applied often result in large energy consumption; efficiency of the process is typically around 70%. The relatively large amounts of steam used in the reforming process (~ 3 as against 1 required by reaction stoichiometry) also decrease the overall process efficiency. The significant heating and cooling steps required to recycle the unconverted steam can explain this. Although high steam to carbon ratios result in high-energy consumption, this is essential to overcome catalyst deactivation due to coke formation. Coking, which is a side reaction in many industrial processes, is a major issue and still needs attention. Besides resulting in catalyst deactivation it also causes serious operational problems [20, 21]. Particularly, Ni is known to be very susceptible to coking. This makes the design of an active and stable catalyst a challenging task. In this context, extensive research has been carried out by Rostrup-Nielsen [15] and discusses coking during steam reforming in detail. Addition of promoters to steam reforming catalysts has been widely reported as a successful tool to improve the catalytic properties in terms of activity and stability [22, 23].

Numerous studies have been reported on the role of potassium [24-26] on the properties of the unmodified catalysts and it is widely accepted that the presence of potassium or other alkali /alkaline earth metals improves resistance to coking by assisting in the formation of OH groups on oxide supports which enhance coke gasification. Formation of OH group is accepted as the intermediate in the breakdown/activation of water and help in the oxidation [27]. Some other authors have

![Figure 3. Equilibrium conversions of methane at temperatures from 450 – 950 °C with steam to carbon ratios (S/C) of 2-4 and pressures of 1, 5 and 10 bar.](image)
reported on the beneficial influence of La as a promoter in the improvement of catalyst stability for reforming reactions [28]. In the case of dry reforming, La is suggested to react with CO₂ forming a new crystalline phase (La₂O₂CO₃) which provides oxygen from its structure and in this way, contributes to coke removal [29, 30]. Additionally, La is known to stabilize metal particles and oxides by being present at the grain boundaries and preventing sintering [31, 32].

In the beginning of last century, naphtha was the most economic feedstock in Europe, in contrast to the natural gas available in United States. Steam reforming of naphtha, light alkanes such as ethane, propane associated with natural gas has also become major industrial route for hydrogen production currently (Eq. 3). In this case, the temperatures required for the process are lower to those applied in steam reforming of methane. This is due to the bond dissociation energies of higher hydrocarbons being lower than those of methane and therefore easier to activate. For the same reason formation of carbon deposits is more severe compared to methane and is one of the main issues. Multiple studies have been performed to elucidate the mechanism of coke formation/growth and to circumvent this bottleneck [33, 34]. A separate catalyst (pre-reforming) is used for the process which operates at much lower temperatures (< 450 °C) [35].

\[
C_{n}H_{m} + nH_{2}O \rightarrow nCO + \left( n + \frac{m}{2} \right)H_{2} \quad (n>1; \text{endothermic reaction})
\]

3.2 Reaction mechanism for steam reforming of methane and higher hydrocarbons

A Langmuir-Hinshelwood type mechanism has been proposed for the steam reforming of methane over supported Ni catalysts [16, 36]. It is commonly agreed, for e.g. in the case of methane, decomposition of methane on nickel surface via C-H rupture is the first step. Subsequently, the carbonaceous species (CHₙ 1 ≤ x ≤ 3) formed on the surface react with steam or surface oxygen species generated by activation of water [30] to produce syngas. Similarly, conversion of higher hydrocarbons takes place by irreversible adsorption to the nickel surface on a dual site, subsequent breakage of terminal C-C bonds one by one until, eventually, the hydrocarbon is converted into C1 components [27].

As for water activation, Rostrup-Nielsen [15] suggested that water is adsorbed and split on the oxide support, e.g. alkali modified aluminas, hydroxylating their surface. OH groups thus formed react with C1 species formed from hydrocarbons to form syngas. In this case, both metal Ni and support oxide provides catalytic sites to activate methane and water, respectively, in a Langmuir Hinshelwood type mechanism involving non-competing sites. Most importantly, these catalytic sites are on metal and the support oxide, thus providing for bi-functional catalysts. Additionally, it has been reported that nickel surfaces are able to dissociate water via nickel oxidation equilibrium (Eq. 4) [15]. Thus, the use of nickel-based catalysts provides additional active sites for water activation and allows for higher steam reforming activities. Similar to the steam
reforming of methane, both metal and oxide supports also participate in the steam reforming of higher hydrocarbons. Such Langmuir Hinselwood type mechanism was proposed by Praharso et al. [36] to describe steam reforming of iso-octane over a nickel-based catalyst.

\[
\text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiO} + \text{H}_2 \quad (\Delta H = 2.12 \text{ kJ} \cdot \text{mol}^{-1})
\] (4)

We have also shown that a bi-functional mechanism is operational for WGS on Pt/ZrO\(_2\) i.e., CO activation takes place on Pt and steam activation on ZrO\(_2\). The reaction occurs at the Pt periphery in close proximity of ZrO\(_2\). Thus catalysts with identical Pt particle sizes give different intrinsic activities (TOF) indicating the role of support [3]. (see figure 4). In mechanistic sequence, activation of water is usually achieved via formation of hydroxyl groups on oxide supports. Hydroxyl groups then react with the “C” residue on the Pt metal to complete SR/WGS reactions [27, 37, 38]. In ceria based supports water activation also occurs via a redox involving the cerium cation. This bi-functional mechanism requires the active metal sites, such as Pt, to be situated in the close proximity of the support OH-groups.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad -41.1 \text{ kJ.mol}^{-1}
\] (5)

The main objective of the WGS reaction (Eq. 5) when coupled with steam reforming is to maximize hydrogen production or adjust the H\(_2\)/CO ratio needed for the end application [27, 48]. It is a well-known reversible, exothermic reaction. Therefore,

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**Figure 4. Turn over frequency of CO over Pt supported oxides.** Condition: dispersion of Pt \(\sim 60 \pm 5\%\), \(P_{\text{CO}} = 60\text{ mbar}\), \(P_{\text{steam}} = 150\text{ mbar}\), \(P = 2\text{ bar}\), \(T = 300°C\), \(GHSV = 2.1\times10^6\text{ h}^{-1}\) (Adapted from Azzam et al. [3])
Chapter 2

CO conversions are favoured at low temperatures. In order to overcome this thermodynamic limitation and thus increase conversions, the WGS of the outlet gas from steam reformer is carried out in multiple stages. The first step (high-temperature shift, HTS) which operates at 300-450 °C is catalysed by Fe-Cr based catalysts. This rather low activity catalyst is also resistant to poisons present in syngas, such as chlorine and sulphur and it acts as a poison trap. Additionally, this catalyst is resistant to adiabatic temperature increase. Since Fe-Cr catalysts have low activity higher temperatures are required to get favourable kinetics. Thermodynamics dictates that the equilibrium towards hydrogen production is unfavourable at high temperatures and thus high temperature shift results in low CO conversions. In order to reach high conversions a second step (low-temperature shift, LTS) which occurs at lower temperatures (180 - 230 °C) over a very active catalyst (Cu-Zn based catalyst) is used [49]. The sensitivity of this catalyst to sintering and sulfur and chlorine poisoning does not make suitable this catalyst to be used by itself in a single step or in the high temperature shift. This two stages approach is not desirable for mobile applications because of its technical complexity. In this respect, extensive research is reported on the design of robust and active catalysts which can be applied in one single stage WGS reactor. Supported precious metal catalysts, e.g. Pt, show promise in this respect [50-52].

4 Steam reforming / gasification of solid biomass

Most of the research and commercial production activities for gasification of solid lignocellulosic biomass based feedstocks draw their inspiration from coal gasification. Gasification can be carried out to equilibrium conversions above 1100 °C. Modern entrained flow gasifiers are operated at elevated pressures (up to 80 bar), temperatures >1250 °C and are designed for coal or oil applications. A comprehensive overview of gasification of dry biomass, reactor types and the problems can be found in excellent reviews on the subject [39, 40]. Bio-oil produced by pyrolysis liquefaction is also considered as a more easy to handle feedstock for gasification [41].

In order to produce a clean tar and methane free syngas at lower process temperatures (<950 °C), various research groups have studied the application of catalysts to biomass gasification. Lowering the temperature of the gasifier below the melting temperature of the ashes reduces equipment costs and allows for gasification at smaller scale compared to entrained flow gasification. Catalysts are either pre-mixed with the biomass, used (partly or fully) as bed material in fluid bed gasifiers or applied downstream of the gasifier for product gas upgrading.

Cheap disposable catalysts have been used to create a valuable fuel gas rather than to produce actual syngas. Dolomite has gained the most attention because it is very cheap [42-45]. It is applied inside the gasifier to promote direct tar cracking or separately in a bed downstream of the gasifier. Although it can almost fully convert tars it is more often used as a tar-reducer, a guard material, allowing the usage of more active but also
more sensitive catalysts downstream [46] However, dolomite is not able to effectively convert methane and suffers from attrition losses [45–47]. Olivine is much more resistant to attrition than dolomite with a somewhat lower activity for tar destruction [47, 48]. Impregnation of the olivine with nickel makes it possible to enhance its activity while maintaining its strength [49] Alkali metals are most effective when impregnated onto the biomass promoting a tar free gas production, especially when potassium carbonate is being used. Catalyst deactivation, catalyst make-up and fluidization problems still need a lot of research attention before these catalysts could be effectively applied [42]. When, in addition to tars also complete methane conversion is desired, high steam (and dry) reforming activity of the catalyst is of vital importance. Ni/Al₂O₃ catalysts have been used in the industry for naphtha and natural gas reforming for many years and since biomass gasification was initially carried out with off the shelf catalysts, it was therefore also logical that they were applied for biomass gasification applications. Caballero et al. [46] and Simell et al. [50] have been able to effectively eliminate the tars in the biomass derived gas and realizing a significant decrease of methane using crushed and/or as-received commercial catalyst or dedicated monolith beds. For complete tar and methane elimination, using downstream secondary reactors after the gasifier have been successful in creating a clean gas. However, up till now none of the proposed processes have reached commercialization.

5 APR of biomass streams

Aqueous waste streams are dilute solutions, typically containing <25 wt% organic molecules. For instance, the aqueous fraction of flash pyrolysis oil commonly consists of 80 wt% water and ~ 20 wt% of a complex mixture of different oxygenates such as aldehydes, ketones, alcohols, acids and sugars [51]. Conventional steam reforming (SR) of aqueous biomass derived streams is economically unfeasible because of their high water contents and the energy required to carry out the reactions in gas phase [7]. Catalytic Aqueous Phase Reforming (APR) is an attractive alternative to produce ‘green’ hydrogen [4, 52, 53]. During APR, water is kept in the liquid phase by applying elevated pressures. Based on system enthalpies, an energy of 3.7 MJ is required to condition 1 kg of water from ambient (25 °C, 1 bar) to gas phase SR conditions (700 °C and 30 bar), while only 2.6 MJ is required to bring 1 kg of water to APR conditions (400 °C and 250 bar). This implies feasibility for APR applications.

Fundamental APR studies are commonly performed with low concentration aqueous solutions of model compounds at temperatures >225 °C and pressures >34 bars [6, 54, 55]. However, reforming of industrially relevant feed concentrations (up to 20 wt% organics) require higher temperatures of 310 - 650 °C (110 – 350 bar) to achieve commercially interesting reaction rates (e.g. residence time in catalytic bed < 5 seconds) [8, 56]. In the future, hydrogen from renewable resources is also projected to partly replace conventional fuels to reduce anthropogenic CO₂ emissions [57]. Hydrogen is expensive and the price depends on the source, e.g. the largest source is refinery hydrogen made mostly from steam reforming of methane and costs around 2200 $/ton.
Chapter 2

The market for hydrogen is expected to grow to 154.74 billion US dollars in 2022 [58]. Air Products is one of the biggest manufacturers of hydrogen and have announced to make hydrogen available for retail at the pump in California for around 10 000$/ton. The integration of the bio-oil refinery with hydrogen production from the aqueous fraction is a promising route to obtain completely green chemicals and fuels. Production of hydrogen by eliminating bio-organic waste streams is very interesting from both economic and environmental viewpoint. Examples detailed below show how hydrogen produced from waste by-product streams in bio-based processes. They allow the hydrogen to be used in the main conversion process and make the whole process totally green.

5.1 APR of waste streams to feedback hydrogen

5.1.1 Example 1 - Isosorbide from Cellulose

Iso-sorbide is a versatile intermediate. It is a potentially useful bio-feedstock, used in pharmaceutical industries e.g., iso-sorbide nitrates for angina pectoris (chest pain), chemicals/polymers e.g., polycarbonates, polyesters [59] and in fuels e.g. diesel additives such as dimethyl isosorbide, or isosorbide di-nitrate as ignition improvers [60]. It is obtained in a two-stage process involving hydrogenation of glucose, which gives sorbitol. Isosorbide is obtained by double dehydration of sorbitol. Hydrogenation of glucose to sorbitol in aqueous media can be achieved at 100 - 120 °C; 20 - 40 Bar H₂ for 120 -180 min with (5wt%) Ru/Carbon catalysts. Ru/Carbon catalyst is very active in glucose hydrogenation to sorbitol with complete glucose conversion and sorbitol selectivity above 98 %. Side products reported are mannitol (below 1%) and gluconic acid (below 0.1 %). [61, 62]; These reactions are carried out in aqueous phase and the by-products formed during the reaction find themselves in the aqueous phase. Sorbitol conversion to isosorbide occurs in two stages with H₂SO₄ as a catalyst. First reaction is performed at 120 °C for 2 h followed by second reaction at 130 °C for 0.5 h. Total conversion of sorbitol is 97.6 % with the following yields: Iso-sorbide – 83.2, 1,4-sorbitan 3.3 and 2,5-sugars, 12.5 %. [63]. In ZnCl₂ solution (70 % in water) sorbitol is converted to iso-sorbide with 85 % molar based yield. At low temperatures the reaction rate is low, with increase in temperature (over 200 °C) the rate improves but extensive amounts of by-products are formed [64]. In the case when a solid catalyst (silico-tungstic acid) isosorbide yield is not higher than 40 % with sorbitans (mixture of 1,4 or 1,5-sorbitan, and 2,5-sorbitan) as the main intermediate products [65].

Thus, the reaction produces a variety of organic molecules dissolved in the aqueous phase resulting in amounts in excess of 12 wt%. Hydrogen required for the reduction of sugars to sorbitol, if obtained from these side products via APR can make the process completely sustainable. For example, 1 mol of sorbitan (C₆H₁₂O₅) can yield 13 mol of H₂ via SR/WGS. One mole of glucose in comparison requires only 1 mol of hydrogen for conversion to sorbitol. Thus, there is enough potential to generate all the required hydrogen for the conversion from the aqueous waste containing by-products.
5.1.2 Example 2 - Humin by-products during sugar to HMF/Levulinic acid conversion

Hydroxymethyl furfural (HMF) and levulinic acid (LA) are addressed as important versatile platform chemicals derived from carbohydrates [66, 67]. A wide range of chemicals used as solvents (e.g., GVL, THF, dimethyl THF), monomers (e.g., furan dicarboxylic acid, caprolactam, adipic acid, etc), and commodity (e.g., butene) can be produced from these platform molecules. The pathways to convert lignocellulosic biomass to the above platform chemicals include separation of carbohydrates from biomass, hydrolysis of these polysaccharides to oligomer/mono carbohydrates (sugars) and dehydration of these sugar monomers (illustrated in Scheme 1.1). Hydrogenation of LA to GVL can be conducted in vapour or liquid phase with high conversion and selectivity using especially Ru catalyst (e.g., 5 wt.% Ru/C, 15 wt% RuRe (3:4)/C, 5 wt% RuSn (3.6:1)/C). Wright and Palkovits have summarised recent advances in catalyst development in their mini-review [68]. Both hydrolysis and dehydration reactions are conventionally performed in aqueous phase using acid catalysts such as HCl or H2SO4 [69, 70]. Yield and selectivity of HMF or LA are strongly dependent on process parameters such as sugar substrates, concentrations, reaction
Scheme 1. Process scheme for GVL derived from cellulose. SEM image of humin adapted from Hoang et al. [76].

temperatures, catalyst etc. However, for most of the potential process configurations, the conversion of carbohydrate substrates to useful products is only about 55 – 65% [71-74]. The rest of carbohydrate is converted to degradation by-products, called humins (50 – 66 wt.% C, 29 – 46 wt.% O and the rest is H) [71-76]. Based on their solubility in the reaction medium, they are further divided into two groups: soluble humins and solid humins. Weingarten et al. [72] reported that for LA from cellulose the selectivity of humins in aqueous phase is approximately from 22 – 80 % (on carbon basis). Thus, the process making LA from biomass can produce large amount of organic waste in aqueous phase. Besides, the solid humin (yield of 25 – 35 wt.%) [71-74, 76] can also be steam reformed to H2 [77]. It is estimated that H2 produced from soluble and solid humin is in surplus to the amount required for hydrogenation of LA to GVL. Thus, they are potentially renewable source for H2 production in bio-refinery and valorisation of humins, carbohydrate-derived wastes, can be achieved.

5.2 Evaluation of this concept in terms of hydrogen economics

Pyrolysis of lignocellulose is a route to liquefaction of solid biomass. Fractionation of the pyrolysis oil in an organic and aqueous phase is the first step in obtaining high value bio-oil. Typical composition of the so obtained bio-oil is given in Table 1. The next step to upgrade involves de-oxygenation of the organic phase with hydrogen. APR of the aqueous phase of pyrolysis oil is an interesting route to produce the required hydrogen for de-oxygenation of the organic phase. A concept for the integration of APR in a bio-refinery is evaluated in terms of hydrogen economics as shown in Table 1 and Figure 6 [51]. In this section, the maximum amount of hydrogen that can be obtained theoretically by APR of the aqueous feed is compared with the amount of hydrogen required to upgrade the bio-oil fraction to commercially relevant hydrocarbons, which can be used in a naphtha cracker to obtain olefins, building blocks
Table 1. Typical composition of bio-oil.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction wt%</th>
<th>Average molecular composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td><strong>Water soluble</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acids, Alcohols</td>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>Ether-solubles</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>Ether-insolubles</td>
<td>30</td>
<td>46</td>
</tr>
<tr>
<td>H2O</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td><strong>Water insolubles</strong></td>
<td>25</td>
<td>66</td>
</tr>
</tbody>
</table>

for chemicals and polymers. It can be seen from Table 1 that 25 wt% of the pyrolysis oil is the desired organic phase. The remaining 75 wt% aqueous phase consists of water soluble compounds (oxygenates + H2O), and is referred to as the aqueous fraction. The oxygenates account for 50 wt% of the pyrolysis oil and these have a weight averaged composition of C=46.8, H= 6.0 and O=47.2 % as shown in Figure 6. The oxygenates in the aqueous phase are ideal feedstock for hydrogen production by APR. Firstly the amount of hydrogen that can be formed during APR of the aforementioned feed is calculated. The assumption is made that maximum hydrogen yields are achieved.

![Figure 6. Amount of hydrogen produced by APR of aqueous phase of pyrolysis oil and the needed amount for upgrading bio-oil.](image-url)
during APR and this implies that (i) all hydrogen atoms in the oxygenate recombine to molecular hydrogen and (ii) carbon undergoes full oxidation by water to form CO₂ and H₂ (WGS). The oxygenates (which represent 50 wt% of the pyrolysis oil) contain 6 wt% hydrogen, indicating that 30 gram (or 15 mol) of H₂ can be produced per kg of initial pyrolysis oil. Furthermore, hydrogen can also be formed by the water gas shift reaction. During WGS, carbon is oxidized by water to form H₂. A single carbon atom can undergo two oxidations by water (C + H₂O → CO + H₂, and CO + H₂O → CO₂ + H₂) and therefore, in the optimal case, two hydrogen molecules can be formed per carbon atom. However, the carbon in the oxygenate molecule is already partly oxidized and this should be taken into account when calculating the maximum hydrogen yield possible. It can be calculated for the oxygenates that the molar ratio of oxygen/carbon is 0.77, while fully oxidized carbon has oxygen/carbon ratio of 2. This indicates that 1.23 molecules of hydrogen can be formed per carbon atom in case of optimal hydrogen yields. Oxygenates are for 46.8 wt% composed out of carbon, indicating that the water-soluble oxygenate fraction (50 wt% of pyrolysis oil) contains ~19 moles of carbon per kg of pyrolysis oil. This indicates that another 23 moles of H₂ can be produced by complete oxidation of the already partly oxidized carbon. The above considerations show that a total of 48 moles of H₂ can be produced maximally from the aqueous fraction of 1 kg of pyrolysis oil. Next, the amount of hydrogen required for upgrading of the organic phase of pyrolysis oil is calculated. The pyrolysis oil is composed of 25 wt% organic phase. During de-oxygenation process, oxygen in the organic compounds is hydrogenated and removed from the molecule in the form of water. Two hydrogen atoms are necessary to remove one oxygen atom in the form of water (O + 2H → H₂O). The oxygen content in the organic phase is 27 wt%, indicating that 68 gram (or 4.2 mol) of atomic oxygen needs to be removed from the organic phase of 1 kg of pyrolysis oil. These calculations show that 4.2 moles of molecular hydrogen (H₂) are necessary to accomplish full de-oxygenation of the organic phase. Bridgewater [78] reported similar relative hydrogen amounts for this process (8 moles of hydrogen to fully de-oxygenate 250 grams of organic phase that was composed of 50 wt% oxygen). Competing side-reactions (e.g. hydrogenation of unsaturated bonds) during de-oxygenation might increase the required hydrogen amounts to achieve full de-oxygenation. It was calculated earlier in this section that maximum H₂ yields of 48 moles could be produced from the aqueous phase of 1 kg of pyrolysis oil. These calculations show that the amount of hydrogen obtained from the aqueous phase is more than enough for full de-oxygenation (ignoring hydrogenation side reactions) of the organic phase, when the hydrogen selectivity for the reforming for the aqueous fraction is at least 10%. The integration of APR to generate hydrogen from the aqueous phase of pyrolysis oil to upgrade the organic phase is graphically presented in Figure 6, and shows this to be conceptually feasible.

5.3 Thermodynamics of APR

Dumesic et al. [79] reported the thermal dependence of the standard Gibbs free energy for water gas shift and steam reforming of various oxygenate molecules in liquid
and vapour phase as shown in Figure 7. A negative value for the standard Gibbs free energy ($\Delta G/RT<0$) indicates that the process is spontaneous. The Gibbs free energy for the water gas shift reaction in liquid phase was reported to be negative and temperature independent in the temperature range 27-375 °C. In the case of vapour phase water gas shift reaction, the reaction becomes less favourable at higher temperatures. The reforming of ethylene glycol, for example, in liquid phase compared to vapour phase becomes more favourable above 175 °C. The advantages of aqueous phase reforming are (i) no need for evaporation of the water and (ii) the water gas shift activity and reforming rates are more favoured in the liquid phase than in the vapour phase at temperatures above 175 °C.

5.4 Why hydrogen is favoured at APR conditions?

Davda et al.[80] have explained why APR conditions favours hydrogen formation. According to them aqueous-phase reforming of oxygenates to produce H$_2$ takes place via steam reforming and WGS. The lowest partial pressure of CO that can be achieved depends on the thermodynamics of the WGS reaction and the operating conditions, [Eq. (6)].

$$P_{CO} = \frac{P_{CO_2}P_{H_2}}{K_{WGS}P_{H_2O}}$$  \hspace{1cm} (6)

![Figure 7. Gibbs free energy for different oxygenates at various temperatures including WGS reaction.](image)
K_{WGS} is the equilibrium constant for the vapour-phase WGS and P_i are partial pressures. Since H_2, CO_2 and small amounts of alkanes (primarily CH_4) are produced by aqueous-phase reforming,[8] gas bubbles are formed within the liquid-phase flow reactor. The pressure in these bubbles can be approximated to be equal to the system pressure, [Eq. (7)].

\[ P_{\text{bubble}} \approx P_{\text{system}} = P_{\text{H}_2\text{O}} + \sum_{\text{products}} P_i \]  

The partial pressures of the reaction products and water vapour are dictated by the feed concentrations, system pressure and temperature, as outlined below. For dilute product concentrations and system pressures above the saturation pressure of water, the bubbles contain water vapour at a pressure equal to its saturation pressure at the reactor temperature, and the remaining pressure is the sum of the partial pressures of the product gases. The extent of vaporization, y, is defined as the percent of water in the vapour phase relative to the total amount of water flowing into the reactor. In contrast, for systems operated at pressures that are near the saturation pressure of water, all the liquid water may vaporize, and the composition of the bubble is dictated by the stoichiometry of the feed stream. At this condition, the partial pressure of water is below its saturation pressure because the reforming product gases dilute the water vapour. Higher concentrations of oxygenate lead to lower partial pressures of water because of greater dilution from H_2 and CO_2 produced by reforming reactions. As the system pressure is increased, the partial pressure of water vapour increases until it reaches the saturation pressure of water, at which point any further increase in the system pressure leads to partial condensation of water. The above arguments indicate that the conditions which favour the lowest levels of CO from reforming of oxygenates are those which lead to the lowest partial pressures of H_2 and CO_2 in the reforming gas bubbles; and, these conditions are achieved by operating at system pressures that are near the saturation pressure of water and at low oxygenate feed concentrations. As the system pressure increases and the extent of vaporization decreases below 100%, the partial pressures of H_2 and CO_2 in the bubble increase, thereby leading to higher equilibrium concentrations of CO. Similarly, as the oxygenate concentration in the feed increases, higher partial pressures of H_2 and CO_2 are developed, even for the case of complete vaporization, again leading to higher equilibrium CO concentrations.

### 5.5 Mechanism of APR / Reaction routes

Catalytic APR studies with model compounds are usually carried out to simplify the process and gain fundamental understanding of catalytic reforming. The purpose of these studies has been to identify pathways that lead to hydrogen and prevent the formation of others. Important reactions during reforming are C-H, C-C and C-O bond cleavages. To prevent alkane formation, it is preferred that every carbon atom is connected to one oxygen atom to enable reforming of the molecule to CO and H_2. Ethylene glycol (EG) is often chosen as a model compound to study fundamental catalytic behaviour because it is the smallest molecule (hence avoiding the occurrence...
of complicated side reactions) with all carbon atoms bonded to oxygen (preventing intrinsic methane formation) where both desired and undesired pathways (C-C, C-O and C-H cleavage) can occur. The reforming of ethylene glycol has been studied intensively by Dumesic and colleagues [6] and a reforming mechanism has been proposed by them as shown in Figure 8. EG first undergoes dehydrogenation leaving adsorbed species on the catalyst surface. The formed intermediate compound can further react through two pathways. The desired pathway to form hydrogen involves C-C cleavage which results in H₂ gas and adsorbed CO. Hydrogen yields is further enhanced by the water gas shift reaction (CO + H₂O → CO₂ + H₂). The undesired pathway involves cleavage of the C-O bond leading to such species as alcohols or rearrangement to form acids. These can further undergo sequential de-oxygenation on metal sites to form alkanes. Other pathways leading to undesired products include dehydration of ethylene glycol to produce vinyl alcohol. Sequential hydrogenation of vinyl alcohol results in the formation of ethanol. Direct hydrogenation of CO₂ can also lead to the formation of CH₄ or even higher alkanes through the Fischer-Tropsch sequence.

5.6 Current status and challenges for APR.

Many APR studies [4, 52, 54, 81, 82] were already undertaken by different research groups to study the reforming of model compounds in subcritical water conditions (175-265 °C and 32-56 bar). These APR conditions are ideal for fundamental reforming
studies; however, reaction rates are relatively slow at these low temperatures and therefore studies are limited to feed solutions of low concentrations or long residence times. The ultimate goal should be to develop a commercially and technologically feasible (catalytic) process for the production of hydrogen by APR of industrial biomass derived aqueous streams that contain complex mixtures (15-25 wt%) of oxygenates. Therefore, much higher reaction rates are required compared to low temperature APR to achieve this goal. Achieving high H₂ yields by reforming of highly concentrated feeds is not only a matter of increasing the catalytic efficiency. Thermodynamics predict an increase in alkane formation for reforming reactions with higher feed concentrations [54]. Production of alkanes should be avoided as it competes with the hydrogen yields. Furthermore, low temperature APR is also reported to be subject to mass transfer limitations, which can severely hinder the catalytic reaction for high feed concentrations. As an example, it was shown by Shabaker and colleagues [5] that APR of ethylene glycol (225 °C and 29.3 bar) with a 3.4 wt% Pt/Al₂O₃ (63 – 125 μm particle size) catalyst was affected by intra-particle mass transfer limitations when an EG feed concentration of 10 wt% was used.

Catalytic supercritical water reforming is promising for achieving high reforming rates and overcome mass transfer limitations. Supercritical water provides a medium with better heat transfer than commonly in gas phase and higher diffusivity than in liquid phase [8, 83]. Guo et al. [8] has published a nice overview of catalytic supercritical water reforming studies of biomass derived compounds. High reaction rates for the reforming of high concentrated oxygenated hydrocarbon streams were reported. However, stability and selectivity issues with the studied catalysts are serious drawbacks for industrial exploitation of this process [8]. Catalyst stability issues in hot compressed water are mainly related to sintering of the supported metal particles [8] or instability of conventional metal oxides catalyst supports (e.g. Al₂O₃, TiO₂ and ZrO₂) [84, 85]. Issues with metal oxide supports are already experienced at low temperature APR conditions [69].

Several authors have discussed the hydrothermal stability of catalysts in APR of model feedstocks [1, 86-88]. Higher polyols feeds can enhance the stability of alumina against dehydration, however under acid feeds the support suffers from severe deactivation. To summarize, the challenge to make sub- or supercritical water reforming of biomass derived waste streams commercially feasible involves the development of catalysts that (i) show high stability in hot compressed water and are stable against different type of impurities and poisons, such as tars, (ii) are able to convert high concentrated feed streams under industrial relevant residence times, and (iii) produce high H₂ yields. A fundamental understanding of the reforming pathways and deactivation mechanisms should help in the development of such catalysts. These issues are addressed below in terms of studies carried out generally by us on model oxygenates.

In general, catalysts for APR should be active for C-C bond cleavage in order to be able to decompose the organic molecules and they should further enhance the Water
Gas Shift (WGS) reaction to maximize hydrogen yields. Methanation and Fischer Tropsch are undesired side reactions, as they consume the desired product, H₂. In order to suppress these reactions, catalysts should not be active for C-O bond breaking [79]. Lower alkane selectivities are therefore expected for catalysts with low affinity towards C-O bond dissociation. In 2003, Davda et al. [79] reported the relative activities of different metals for C-C, C-O bonds dissociation, and for WGS reaction. They reported high C-C bond breaking activities for Ir, Ru and Ni. Therefore, these metals might be promising catalysts for breaking down oxygenates. Adsorbed oxygenate fractions on the catalyst surface resulting from C-C bond dissociation can undergo dehydrogenation, yielding H₂ and CO [79]. Follow-up reactions, such as methanation and WGS, strongly control the final hydrogen yield. Ir showed very low methanation activity but in contrast to Ru and Ni, almost no WGS activity was reported. Furthermore, Ru and Ni have been reported to have high activities for methane formation [79].

Catalytic reforming of ethylene glycol (5 & 15 wt%) in supercritical water (450°C and 250 bar) in the presence of alumina supported mono- and bi-metallic catalysts based on Ir, Pt and Ni has been reported [56]. Pt catalyst showed the highest hydrogen yields compared to Ir and Ni. Varying the Pt loading (0.3 - 1.5 wt%) showed that the intrinsic reforming activities improved with decreasing Pt loadings as shown in Table 2. However, a lower Pt loading had a large negative effect on the H₂ selectivity and catalyst stability. It was found that the presence of Ni in a Pt-Ni bimetallic catalyst improved hydrogen yields by suppressing methane formation. Moreover, the presence of Ni also enhanced catalyst stability. Results reported here were obtained at WHSV of 18 h⁻¹. The Pt-Ni/Al₂O₃ having a total metal loading of 1.5 wt% (molar ratio Pt:Ni = 1), is identified as a promising catalyst for the reforming of ethylene glycol in supercritical water.

The bi-functional reforming mechanism involved with APR over alumina supported Pt catalysts requires water activation. Water activation happens on the alumina support through the formation of hydroxyl groups. Smaller Pt particles were

**Table 2. Experimental data for 15 wt% ethylene glycol reforming (WHSV 17.8h⁻¹) at 450°C and 250 bar using 0.3, 0.6 and 1.5wt% Pt supported on γ-alumina (Adapted from De Vlieger et al. [9])**

<table>
<thead>
<tr>
<th></th>
<th>0.3wt% Pt</th>
<th>0.6wt% Pt</th>
<th>1.5wt% Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon to gas (%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>48</td>
<td>42</td>
</tr>
<tr>
<td><strong>Carbon in liquid (%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>59</td>
<td>61</td>
</tr>
<tr>
<td><strong>Selectivity (%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>42</td>
<td>51</td>
<td>80</td>
</tr>
<tr>
<td>CO₂</td>
<td>50</td>
<td>60</td>
<td>79</td>
</tr>
<tr>
<td>CO</td>
<td>20</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Alkanes</td>
<td>30</td>
<td>26</td>
<td>7</td>
</tr>
</tbody>
</table>
found to give higher intrinsic reforming activities due to a larger interfacial (metal/support) area, which enabled better interaction between the reforming fragments on the Pt and the hydroxyl groups on alumina support. Positive effect of smaller Pt particle size on dehydrogenation and decarboxylation activity has also been reported by the group of Lercher [89].

On the other hand, we have shown earlier smaller Pt particles were found to be responsible for lower hydrogen selectivities due to increased methane formation. Methane can be formed by either dehydration of EG and/or by the hydrogenation of COx. Pt-Ni bimetallic catalyst shows enhanced hydrogen yields by suppressing methane formation. The new Pt-Ni catalyst also shows two times more activity compared to a monometallic Pt catalyst due to supposed lower CO coverage caused by the presence of Ni and an enhanced accessibility to Pt sites for reforming. Moreover, the addition of Ni also enhanced catalyst lifetime and stable catalytic performances were observed for the reforming of ethylene glycol under supercritical water conditions.

For the reforming of methanol, a selectivity of 8% towards CH4 was observed for the Pt catalyst. Formation of alkanes during the catalytic reforming of 1 wt% acetic acid, methanol and ethanol along with conversions to gas phase at 275 °C and 200 bar are shown in Figure 9 [1]. The selectivity towards alkanes (mainly methane) was found to be the highest (±47%) during acetic acid reforming. In the case of ethanol reforming the Pt catalyst showed CH4 selectivity of ±20%. The higher amounts of methane observed during ethanol reforming is attributed probably to the CHx fragment formed by C-C bond breaking of ethanol [90] on the Pt surface. CHx fragments can recombine with adsorbed H atoms on the Pt surface to form methane. A similar sequence is also suggested for acetic acid on Pt based catalysts [91, 92]. In the case of methanol, C-O bond breaking is necessary to generate these adsorbed CHx species that lead to the production of methane. High C-C bond breaking activities for Pt during reforming of ethanol and low activity for C-O bond breaking [79] during reforming of methanol can explain the observed differences for methane formation.

For methanol reforming with the Pt-Ni catalyst almost no methane was formed. Methanol was found to be one of the major products during the reforming of EG which explains why Pt-Ni/Al2O3 catalyst shows almost no methane formation in agreement with earlier studies [6] and previous results in our research group [56]. The lower methane production observed during methanol reforming in the presence of Pt-Ni can be explained by the enhanced dehydrogenation activity of Pt-Ni catalyst [93], favouring C-H cleavage instead of C-O cleavage in methanol. Promoting the Pt catalyst with Ni did not affect the alkane (methane) selectivity for acetic acid or ethanol reforming as can be expected from the reforming routes. Reforming of these compounds inherently lead to CHx species on the catalyst surface, which is a precursor for methane formation. In case of methanol reforming, the intermediate CHxO must undergo C-O cleavage to form CHx (and hence methane). Methane formation during methanol reforming can be
Figure 9. Alkanes selectivity for catalytic reforming of acetic acid, methanol and ethanol at 275°C/200bar. Conversion levels are shown above the selectivity values (Adapted from De Vlieger et al. [1])

Prevented by avoiding C-O cleavage. Reforming experiments with 1 wt% methanol (Figure 10A) and ethanol (Figure 10B) solutions showed stable activity levels for both Pt and Pt-Ni catalysts. Catalysts used for acetic acid reforming deactivated during the reaction (Figure 10C). Both catalysts showed similar deactivation rates. The catalysts lost all activity after 3 hrs on stream with final conversion levels (~5%) being similar to the reforming experiment without a catalyst. Deactivation of the catalyst with acetic acid is commonly observed in reforming reactions [91]. The formation of methane resulting from acetic acid decomposition is reported in literature to be a possible cause for deactivation of catalysts [94]. It is suggested that C-H bond breaking in methane further results in CHx species (1≤x≤2) on the catalytic surface. These fragments can further oligomerize to coke species [91]. However, catalysts used for ethanol reforming were found to be stable while also producing high amounts of methane (20%). It is also known that Pt and Ni catalysts are stable for the reforming of methane. Therefore, it is concluded that methane-induced deactivation is unlikely and the dominant deactivation pathway is due to other causes [1, 56]. Further, liquid products formed during the APR of acetic acid, methanol and ethanol were investigated to find any role for them in catalyst deactivation. During acetic acid reforming, a conversion of 7% to liquid by-products was observed for the Pt catalyst. By products were identified as formaldehyde and iso-propanol. For ethanol, a conversion of ±6% to liquid by-products was found for the Pt catalyst. The main product was acetic acid, and the remaining was acetaldehyde (<0.5%). The Cannizzaro reaction (disproportionation of an aldehyde to alcohol and carboxylic acid) could be responsible for some of the acetic acid formed during ethanol reforming. The Pt and Pt-Ni catalysts studied did not influence the
amount of acetic acid and acetaldehyde formed during ethanol reforming, while during EG reforming, the amount of acetic acid was strongly dependent on the type of catalyst. This shows that the Cannizzaro-derived reaction is not a dominant contributor to acetic acid formation during EG reforming. Aqueous phase reforming experiments with liquid products formed during the APR of EG was carried out using individual components (Figure 10).

![Graphs showing conversion of methanol, ethanol, and acetic acid over different catalysts](image)

**Figure 10.** Carbon to Gas conversion of A) methanol, B) ethanol and C) acetic acid over 1.5 wt% Pt/Al₂O₃ and 1.15 wt% Pt-Ni/Al₂O₃ [1].

30
Reforming experiments (with acetic acid, methanol, or ethanol) were conducted at 275 °C and 200 bar in the presence of Pt/Al₂O₃ or Pt-Ni/Al₂O₃. Feed concentrations of 1 wt% were used so as to work in the same concentration range as the liquid by-products formed during EG reforming experiments. For example, a total conversion of 15% to methanol, ethanol and acetic acid was observed during the reforming of 20 wt% EG, resulting in a total concentration of 3 wt% liquid by-products.

FT-IR spectra of the used catalysts were subtracted from each other as shown in Figure 11 to study differences in chemical groups on the surfaces of the used Pt catalysts. Subtracting the spectrum of the catalyst that was exposed to only water from that of aqueous methanol solution resulted in a more or less flat line, indicating that the surface composition of the active catalysts (used for methanol and water only) are similar. Subtracting the spectrum of the catalyst subjected to only water from the spent deactivated acetic acid catalyst resulted in 3 strong bands; one lattice vibration in the region 1000-1200 cm⁻¹ and two sharp OH related bands located at 1975 and 2112 cm⁻¹. Also in the FT-IR spectra, the acetic acid treated sample showed the highest O-H intensity (Figure 11). These results indicate the presence of a highly hydroxylated type of Boehmite in the acetic acid deactivated catalyst compared to the active catalyst used in methanol APR.

Acetic acid was shown to be responsible for the deactivation of Pt and Pt-Ni catalysts by hydroxylation of the Al₂O₃ surface. Re-deposition of the dissolved alumina on the catalyst leads to the blocking of catalytic Pt sites (see Figure 12) and hence deactivation of the catalyst [1]. The increased dehydrogenation activity of the Pt-Ni

![Figure 11. FT-IR spectra of 1.5wt% Pt/Al₂O₃ catalyst used for APR of acetic acid, methanol and only water (275 °C and 200 bar) [1].]
catalyst was found to suppress the formation of acetic acid during ethylene glycol reforming and thereby increasing the H₂.

Stability issues of catalyst support materials in SCW are a major setback for these reactions and stall the further development and industrial exploitation of this technique. The development of stable catalytic support materials for reactions in SCW is therefore of much importance. Carbon nanotubes (CNT) are widely recognized for their significant physical and chemical stability, high heat conductivity and open structure. These properties are already explored for different applications. We have shown that CNT to be a promising stable catalyst support material for reactions in SCW [2]. The efficiency of Pt/CNT as catalyst for the production of hydrogen by reforming of ethylene glycol and acetic acid in SCW was studied and illustrated the applicability of CNT as catalyst support in SCW (Figure 13).

5.7 APR for green chemicals

Lignin comprises of 10 – 40 wt.% of lignocellulose [69, 95]. Currently, lignin is produced in paper industry as the by-product of pulping process where it is mainly used for combustion to generate heat, steam and electricity. As constructed from methoxylated phenyl propane units, lignin has been addressed as a potential resource for bio-derived aromatics [96-98]. The solubilisation and conversion of various types of lignin (e.g., kraft lignin, Acell organosolv lignin, soda lignin) in mild liquid phase reforming (LPR) condition (i.e., T ~ 225°C P ~ 25 – 58 bar) were explored by Weckhuysen et al. [99]. Among these lignin feedstock investigated in their study, the solubility followed the order Acell organosolv > Soda > Kraft. About 93 wt.% of lignin could be dissolved in compressed water at 225°C meanwhile only 38 wt.% of kraft lignin dissolved under the same conditions. However, the average molecular mass (Mₐ) of the depolymerized lignins were still above 2000 Da and the decrease of Mw varied from 22 – 57 % [97, 99]. Co-solvents (e.g., ethanol, formic acid and phenol etc.) and co-catalysts such as NaOH or H₂SO₄ were reported to help improving the monomer yields due to
Figure 13. Conversion and gas phase selectivities of 5 wt% ethylene glycol reforming in super-critical water (450°C and 250 bar) using Pt-CNT catalyst (Adapted from De Vlieger et al. [2])

enhancement of lignin solubility and preventing re-condensation of lignin fragments [97, 99-102]. In addition, the co-solvents are also partially reformed under the liquid phased reforming conditions, producing H₂ which in turn contributes to the hydrogenolysis and hydro-de-oxygenation of lignin. The conceptual process for lignin valorization via LPR was later proposed and illustrated in Figure 14 [100]. The products (Figure 15) include oil type soluble aromatics, insoluble char and gases (e.g., CO₂, alkane, H₂ etc.) [98]. At subcritical and supercritical water conditions, catechol yield peaked at short retention times then it gradually decreased while the yields of phenol and cresols increased along time on stream [98, 103]. Condensation or polymerization reactions were also observed, resulting in higher mass molecules and further insoluble products [97, 98, 102]. At subcritical conditions, the yield of solid products varied from ~10 to ~60 wt.% depending on the temperatures, catalyst used, retention time [98, 102-104]. The solid char can also be used as feedstock for steam reforming for hydrogen. Various noble or transition metal supported catalysts have been tested for the reaction (e.g., Pt/Al₂O₃, Ru/C, Pd/C). Although Al₂O₃ support is notorious for phase transition to boehmite under APR condition, its stability was enhanced with the presence of lignin[88]. The authors attributed this stability improvement to the interactions of oxygen functionalities of lignin with the support.
Figure 14. Valorisation of lignin via liquid phase reforming produces aromatic chemicals, gas and valuable solvent (Adapted from Zakzeski et al. [98])
Figure 15. Product distribution after treatment of lignin in near and supercritical water at 30 MPa and 350 °C (a) and 400 °C (b), respectively. MS – Methanol soluble products MI – methanol insoluble products (Adapted from Wahyudiono et al. [97])
5.8 Challenges for the future

As outlined in this chapter the feasibility of APR has been shown to be possible with model molecules, for example sorbitol [87, 105]. For instance, Virent has patented process to produce liquid fuels from sugar derivatives by incorporating in-situ hydrogen production by APR [106]. Sorbitol transformations to fuels with industrial respects is discussed thoroughly in recent review [107]. The conceptual process is still in research stages in laboratories. This is because studies have been with simplistic molecules such as methanol, ethanol, poly-ols (glycols, glycerol), acetic acid etc., in reality aqueous waste streams contain complex mixtures of organic molecules. However, studies on model systems have provided for a good understanding of requirements for efficient catalyst design. Catalysts are mandatory for the development of an efficient APR process. Research work carried out in various groups has provided for this knowledge and this is a positive and good start.

However, a variety of scientific and technological questions have still to be answered. In the case of catalysts achieving long-term stability is of paramount importance. Severity of conditions used in APR is problematic due to sintering and loss of active surface area of supports and metal phases, as well as leaching. The other major problem to be solved for APR is the tendency of the organic molecules, which are very reactive and can undergo a variety of reactions. Some of these also result in secondary oligomerization/condensation reactions, which lead to severe coking and subsequent blockage of catalytic sites and catalyst deactivation. Bio-oxygenates also have a severe tendency to form homogeneous char in the reaction medium and heterogeneous char on the catalyst. Efficient catalysts should minimize heterogeneous char as well as have the ability to gasify homogeneous char. However, the problem of homogenous char in our opinion cannot be solved by catalyst development alone. Smart reactor and feed injection nozzle into the reactor system are critical. Developments in feed systems for turbines have faced similar issues and such knowledge can be applied. In conclusion, Aqueous Phase Reforming is a promising concept with potential for commercial development.

6 References


Chapter 3

Experimental techniques

In this chapter, the catalyst preparations with detailed characterization techniques are explained. The setup for the APR studies is described with the equipment used for product analysis. Furthermore, the means of determining catalyst performance along with definitions used are discussed.
1 Catalyst preparation

This study employed Pt catalysts supported on different materials. The materials were mesoporous Carbon (C), Boehmite (AlO(OH)) and Zirconia (ZrO₂). The catalysts were prepared by using different methods such as incipient wetness impregnation, wet impregnation, microemulsion technique. For each study presented in this thesis the details of preparation methods and other specific characteristics are discussed in the corresponding chapters.

In order to understand the functioning of the catalysts in relation to their physical characteristics, catalysts studied have been characterised with a variety of techniques. These are detailed below.

2 Catalyst characterization

For characterization of the fresh and spent catalysts the following methods were applied:

**XRF Analysis:** The metal loading on the catalysts were analyzed with X-ray Fluorecence (XRF) spectroscopy using Bruker S8 Tiger with 4 kW Rh source. Quantexpress semi-quantitative method was applied. First, catalysts were measured qualitatively as powders (approximately 0.1 g) in order to confirm elements present in the samples. Catalysts were then pressed into pellets in a 13 mm die. For carbon supported catalysts a 0.5 ml of binder of 50 g/l solution of Elvacite, (C₈H₁₈O₂) dissolved in acetone was used corresponding to 25 wt% binder in the sample. Catalysts studied in Chapter 6 were analyzed at Boreskov Institute of Catalysis using the following method: Semi-quantitative analysis of metal concentrations was performed using wavelength dispersive X-ray fluorescence (WDXRF) spectrometry with the powder pellet method. Undiluted samples (0.5 g) were milled and put in the 29 mm diameter die. The intensities of the metal lines in the samples were measured in vacuum conditions on an ARL Advant’X spectrometer equipped with a Rhodium anode X-Ray tube. Excitation conditions were as follows: tube voltage of 50 kV; current of 40 mA; collimator with a divergence of 0.25°; LiF200 crystal was used as a monochromator; scintillation counter was used as a detector; counting time was 12 s. Contents of elements in the sample were estimated using semi-quantitative method by means of a QuantAS program for standardless analysis.

**BET surface area:** Specific surface areas of the catalysts were measured using N₂ physisorption using the BET adsorption isotherm (Micromeritics, Tristar 3000).

**Chemisorption:** Pt metal surface areas / dispersions were determined by pulse CO or pulse H₂ chemisorption with Micromeritics ChemiSorb 2750 equipment at room temperature (RT). Chemisorption prodecure was as follows. The catalyst samples were pretreated by flushing with Helium (CO chemisorption) or Argon (H₂ chemisorption) at
RT for 20 minutes and then heating up (5 °C/min) in H\textsubscript{2} to 200 °C and kept in this temperature for 1 hour. Catalysts were flushed with the corresponding inert gas for 30 minutes before cooling down to RT (5 °C/min) and start of the pulse chemisorption. Dispersions were calculated based on volume of adsorbed gas; for CO as 1:1 ratio to Pt and for H\textsubscript{2} 2:1 ratio to Pt assuming Pt as hemispherical shaped particles.

**TEM imaging:** Transmission Electron Microscopy (TEM, Philips 300kV, equipped with energy-dispersive X-Ray spectroscopy (EDX)) was used to record Pt size distributions and Pt sizes. Approximately 250 particles across 10 different spots on each sample were measured to give a weighted average size.

**XRD analysis:** X-ray diffraction (XRD) patterns were collected by Brooker D2 Phaser over the range 2\(\theta\) = 10-90° using CuK\(\alpha\)1 radiations source.

**Elemental analysis:** The elemental composition of the spent, oxide supported catalysts were determined using a Perkin-Elmer Elemental Analyser (Thermo Scientific Flash 2000). Approximately 3-4 mg of sample was used for the analysis. Concentrations of C, H and N were calculated based on amounts of water, CO\textsubscript{2} and N\textsubscript{2} evolved from decomposition of the sample in 35 vol. % O\textsubscript{2}/Ar flow (390 ml/min) at 900 °C. Acetanilide was used for calibration, and oxygen content was calculated based on the mass balance.

**PZC measurement:** Point of zero charge (PZC) was measured at different pH values combining Laser Doppler Velocimetry (LDV) and Dynamic Light Scattering (DLS) using a Malvern Nano-ZS Zetasizer. The zeta potentials were determined by the Smoluchowski approximation.

**XPS analysis:** X-ray Photoelectron Spectroscopy (XPS) was used to determine elemental composition of catalyst surfaces. Measurements were done with Quantera SXM (Physical Electronics) with an AlK\(\alpha\) monochromatic X-ray source (1486.6 eV).

**TPO analysis:** Temperature Programmed Oxidation (TPO) was used to measure type and composition of coke deposits on spent oxide supported catalysts. Samples (3-4 mg) were pretreated in He (25 ml/min) at 150 °C for 30 min. After cooling down to 25 °C the samples were oxidized in 5 vol. % O\textsubscript{2}/He mixture (25 ml/min) while heating to 600 °C with a heating rate of 5 °C/min. An online methanizer (Model 110 Chassis, SRI Instruments Europe GmbH) was used to convert CO and CO\textsubscript{2} formed during TPO, to methane using a Ni catalyst. The amount of methane formed was quantified with an FID detector. Al\(_2\)(CO\textsubscript{3})\(_3\) was used for calibration of the FID.

**Catalyst regeneration** was done by oxidizing the samples (oxide supported catalysts only) under 11% O\textsubscript{2} at 300 °C for 2 hours, heating rate 5°C/min.

**Pyridine FT-IR spectroscopy:** Catalysts surface acidity were determined by using Fourier Transformation Infrared Spectroscopy (FT-IR) of adsorbed pyridine. Measurements were conducted in a Bruker IFS 66 IR spectrometer equipped with HgCdTe detector (4000-650 cm\(^{-1}\), 2 cm\(^{-1}\) resolution, 32 scans). Prior to pyridine
adsorption at room temperature, self-supporting wafers of the studied catalysts (5
ton/cm², 20 mg, 1 cm²) were degassed under vacuum (10⁻³ mbar) for 2 h at 200 °C. Gaseous and weakly adsorbed pyridine was removed by evacuation for 30 min at 25 °C. Subsequently, catalysts were treated at 225 °C for 60 min to evaluate the adsorption strength of chemisorbed pyridine.

**ATR-IR spectroscopy:** Attenuated Total Reflection - Infrared Spectroscopy (ATR-IR) was used to study adsorbates on the catalyst surface (only oxide supported catalysts) in gas phase and under APR conditions. Spectra were collected using FT-IR spectrometer (Bruker, Tensor 27) equipped with liquid nitrogen cooled MCT detector and ATR-IR Tunnel cell (Axiom) mounted in sample chamber. Every spectrum was recorded with 4 cm⁻¹ resolution averaging 256 scans for background spectra and 128 scans for liquid and gas phase spectra. An internal reflection element (ZnSe rod, diameter 6.4 mm, length 70 mm) was spray-coated with catalyst and carefully placed inside the tunnel cell using O-rings (Kalrez 7075). The cell was connected to gas or liquid inlet. Schematic representation of the setup is shown in Supplementary information - Chapter 3. Pre-treatment of the catalyst layer was done in He (20 ml/min) at 150 °C in order to remove any solvent traces used during catalyst immobilization. The sample was oxidized in 40 vol% O₂/He mixture (50 ml/min) at the same temperature and cooled down to room temperature in 50 vol% H₂/He flow (50 ml/min). CO gas phase adsorption was done at room temperature during 1 hour in a 20 vol% CO/He mixture (25 ml/min). In liquid phase experiments, degassed water was pumped (1 ml/min) into the system until 40 bar by HPLC pump (Dionex P680) and heated to APR temperatures (150-210 °C). The catalyst was first heated to 150 °C, followed by stepwise further heating with 10 degrees, keeping the sample in isothermal for 30 minutes at each step. Spectra were recorded in the end of each step.

**NH₃-TPD measurement:** Temperature-programmed desorption of ammonia (NH₃-TPD) was performed in a Autochem 2910 II instrument from Micromeritics. The samples were pretreated in He (50 ml/min) at 200 °C for 1 h. NH₃ adsorption was performed at room temperature for 30 min, followed by removal of physisorbed NH₃ in He flow for 1 h. Desorption of NH₃ was monitored in the range of 20-600 °C using a heating rate of 10 °C/min.

### 3 Experimental setup for catalytic measurements

The experiments conducted in this study were performed with a fixed bed continuous flow reactor. After the experiments reported in Chapter 4 few modifications were made mainly to facilitate better sampling during the experiments. These changes are explained in detail in Supplementary information – Chapter 3. Scheme of the setup used in Chapters 5, 6 and 7 are shown in Figure 1.

The experiments were started by introducing the feed via a syringe pump at the desired flow rate (1-2 ml/min) through the preheater to the reactor (L= 63 cm, φ=0.7 cm)
in which the catalyst was placed. The feed used was either ethylene glycol (EG) or hydroxyacetone (HYDA) with concentrations ranging from 2 to 5wt%. The liquid feed was flown through the system, typically from 30-45 minutes, to flush air out of the system. Subsequently, the system was pressurised to the desired level using the back-pressure regulator (BPR). Once the target pressure was reached, heating of the system was started. Reaching operating temperature took approximately 30 minutes and another 30-60 minutes was allowed for stabilization before collecting data. The reactor effluent was cooled down to room temperature with a heat exchanger prior to passing through the BPR. As pressure was released by BPR, liquid and gas separated and travelled via outlet tube to sampling vessels (home-made, volume of liquid collection 9 ml and gas collection 8 ml) equipped with sampling lines. Gas composition, carbon content in liquid and liquid composition were measured at this point (details given later). To the outlet tube $N_2$ gas was introduced as a standard with a flow rate of 10 ml/min to allow accurately analyze the gas composition and gas flowrate. From the sampling vessel, the gas and liquid streams went via collection bottle placed on a balance. Liquid was collected here and the liquid effluent flowrate was calculated by measuring the weight of the liquid over a time assuming density of liquid water at room temperature. The gas produced travelled further through a mass flowmeter (MFM, Brooks GF40) and then to a vent. Gas flowrate ($V_{N_2}$) was measured as $N_2$ with the MFM and converted to individual gas component’s flow volumetric rate ($V_n$ ml/min) using a gas conversion factor (GCF). This calculation is shown in Equation 1, in which $p_n$ is partial pressure of the gas, GCF is the gas conversion factor and $V_{N_2}$ is the gas flowrate measured as $N_2$.

$$V_n = p_n \times GCF \times V_{N_2} \quad (1)$$

The partial pressure of each gas component was obtained by measuring the composition of the gas by micro-GC (Varian CP-4900) equipped with MS5 and PPQ columns. The standard gas ($N_2$) was used to calculate the partial pressure for each gas component. As the MFM was calibrated for $N_2$ at 0°C and at 1.0133 bar a gas conversion factor was calculated (Eq. 2) and corrected to analysis conditions (Eq.3). In Equation $s_n$ is the molecular structure factor for the individual gas component $n$, $d_n$ is the standard density of the gas component and $c_{p,n}$ is the specific heat of the gas component. The possible gasses present in the mixture were: $1, \ldots, n = H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8$. The used densities, specific heats and molecular structure factors are presented in Table 1. In Equation 3, $T_x$ is the temperature in analysis conditions (22 °C, 293 K) and $T_2$ is the temperature of calibration of the MFM (0 °C, 273.15 K).

$$CGF = \frac{d_{N_2}c_{p_{N_2}}(p_1s_1+p_2s_2+\ldots+p_ns_n)}{p_1c_{p_1}+p_2c_{p_2}+\ldots+p_nc_{p_n}} \quad (2)$$
Chapter 3

Table 1. Densities, specific heats and molecular structure factors used for calculation of GCF.

<table>
<thead>
<tr>
<th>Component</th>
<th>Density ( d )</th>
<th>Specific heat ( c_p )</th>
<th>Molecular structure factor ( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>0.0899</td>
<td>3.4190</td>
<td>1.000</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>1.2500</td>
<td>0.2485</td>
<td>1.000</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>1.2500</td>
<td>0.2488</td>
<td>1.000</td>
</tr>
<tr>
<td>( \text{CO}_{2} )</td>
<td>1.9640</td>
<td>0.2016</td>
<td>0.941</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>0.7150</td>
<td>0.5328</td>
<td>0.880</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>1.3420</td>
<td>0.4097</td>
<td>0.880</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>1.2600*</td>
<td>0.3473</td>
<td>0.880</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_8 )</td>
<td>1.9670</td>
<td>0.3885</td>
<td>0.880</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6 )</td>
<td>1.8770</td>
<td>0.3541</td>
<td>0.880</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0.0005*</td>
<td>1.0080</td>
<td>0.941</td>
</tr>
</tbody>
</table>

All constants at 0 °C and 1.0133 bar, source[1]

*source [2]

**source [3]

Temperature Corrected CGF = \( \text{GCF} \times \frac{T_x}{T_s} \)  \( (3) \)

Further, the flowrate was converted to molar flow rate \( \left( F_n \right) \) according to ideal gas law (Equation 4) in which \( R \) is the gas constant and \( T \) is the room temperature (22 °C, 293 K).

\[
F_n = \frac{p_n V_n}{R \times T} \quad (4)
\]

Carbon content in the liquid effluent stream was measured by Total Organic Carbon analyzer (TOC, Shimadzu TOC-V<sub>C</sub>SH Analyzer) for experiments in Chapter 4 and 5. And later on Perkin-Elmer elemental analyzer (Thermo Scientific Flash 2000) was used. For the latter, approximately 3-4ml of each sample was used for the analysis.

Concentration for carbon was calculated based CO<sub>2</sub> from decomposition of the sample in 35 vol.% O<sub>2</sub>/Ar flow (390 ml/min) at 900 °C. Acetanilide was used for calibration, and oxygen content was calculated as rest. Composition of the liquid stream was analyzed with Shimadzu High Pressure Liquid Chromatogram (HPLC, RID-10A detector, Aminex HPX-87H column, 300×7.8 mm) in 0.005 M H<sub>2</sub>S<sub>4</sub> effluent, flow of 0.6 ml/min.
4 Definitions

The definitions and calculations used in the studies for this thesis are described below. The performance of the catalyst is presented as i) Total Carbon conversion, ii) Carbon to Gas conversion, iii) selectivity or yield, iv) rate of reaction and v) turnover frequency (TOF).

Conversion of studied oxygenate \( s \) (\( s= \) EG or HYDA) to gaseous and liquid products was measured in terms of Total Carbon conversion \( (X_{t,s,i}) \) at different times of reaction \( (i=30, 60, 90, \ldots, \text{min}) \) based on Equation 4. Concentration of \( s \) in the feed \( (C_s, \text{mol/ml}) \) was multiplied by the liquid feed flowrate \( (V_{\text{feed}}, \text{ml/min}) \) to get molar flow rate of the feed \( (F_s) \). The same was done for the effluent flow by multiplying the measured concentration of \( s \) at the given times of reaction \( (C_{s,i}^{\text{out}}, \text{mol/ml}) \) by the averaged flowrate of the liquid effluent \( (V_{LQ}^{\text{out}}, \text{ml/min}) \). The molar flow rate of \( s \) from the reactor \( (F_{LQ}^{\text{out}}, \text{mol/min}) \) was the subtracted from the molar flow rate of the feed \( (F_s, \text{mol/min}) \). The difference was then divided by the molar flow rate of the feed. The calculations are illustrated in Equation 5.

\[
X_{t,s,i} = \frac{C_s \cdot V_{\text{feed}} - C_{s,i}^{\text{out}} \cdot V_{LQ}^{\text{out}}}{C_s \cdot V_{\text{feed}}} = \frac{F_s - F_{LQ}^{\text{out}}}{F_s} \times 100
\]  

(5)

Carbon to Gas conversion \( (X_{C2G,i}) \) was used to estimate the gasification efficiency of the catalysts. This was done by measuring the carbon concentration in the feed \( (C_{\text{carbon},i}^{\text{in}}, \text{mol/ml}) \) and in the liquid effluent \( (C_{\text{carbon},LQ,i}^{\text{out}}, \text{mol/min}) \) and multiplying them with the corresponding flowrates, \( V_{\text{feed}} \) (ml/min) and \( V_{LQ}^{\text{out}} \) (ml/min), respectively. The resulting molar flow rates, \( F_{\text{carbon}}^{\text{in}} \) and \( F_{\text{carbon},LQ,i}^{\text{out}} \) were then subtracted from each other and the result divided with \( F_{\text{carbon}}^{\text{in}} \) as shown in the Equation 6.

\[
X_{C2G,i} = \frac{C_{\text{carbon},i}^{\text{in}} \cdot V_{\text{feed}} - C_{\text{carbon},LQ,i}^{\text{out}} \cdot V_{LQ}^{\text{out}}}{C_{\text{carbon},i}^{\text{in}} \cdot V_{\text{feed}}} = \frac{F_{\text{carbon}}^{\text{in}} - F_{\text{carbon},LQ,i}^{\text{out}}}{F_{\text{carbon}}^{\text{in}}} \times 100
\]  

(6)

Carbon to Liquid conversion \( (X_{LQ,i}) \) was calculated to understand how much carbon was lost to the liquid phase by inefficient gasification. Using already established \( F_{\text{carbon}}^{\text{in}} \) and \( F_{\text{carbon},LQ,i}^{\text{out}} \), the carbon concentration in the product gas \( (C_{\text{gas},i}, \text{mol/ml}) \) was multiplied by the averaged flowrate at the time intervals for measurement \( (V_{\text{gas},i}, \text{ml/min}) \). The calculation is presented in Equation 7.

\[
X_{LQ,i} = \frac{F_{\text{carbon}}^{\text{in}} - F_{\text{carbon},LQ,i}^{\text{out}} - C_{\text{gas},i} \cdot V_{\text{gas},i}}{F_{\text{carbon}}^{\text{in}}} \times 100
\]  

(7)
Carbon balance was calculated as in Equation 8. Identified carbon in liquid phase (measured by HPLC) \( F_{\text{out,HPLC}}^{\text{carbon,LQ},i} \) was multiplied with the total in total carbon in the liquid phase (measured by the CHN analyzer) and then added to carbon flow in the gas phase \( F_{\text{carbon,gas},i} C_{\text{gas},i} * V_{\text{gas},i} \) and possible coke \( F_{\text{coke},i}, \text{mol/min} \). The amount of coke is estimated based on carbon deposits on the catalyst at the end of the reaction and then divided by the time of reaction to create an estimate of the coking speed. The sum of these values was then divided by the sum of total carbon in liquid phase and carbon flow in the gas phase and coke on the catalyst.

\[
CB_i = \frac{F_{\text{out,HPLC}}^{\text{carbon,LQ},i} C_{\text{carbon,LQ},i} + F_{\text{carbon,gas},i} C_{\text{gas},i} + F_{\text{coke},i}}{F_{\text{carbon,LQ},i} C_{\text{carbon,LQ},i} + F_{\text{carbon,gas},i} C_{\text{gas},i} + F_{\text{coke},i}} \times 100
\]  

Selectivity shows how well the catalyst performed for the desired reaction. Hydrogen selectivity \( S_{H_2,i} \) was calculated as in Equation 9. The produced hydrogen molar flowrate \( F_{H_2,i}, \text{mol/min} \) was divided with converted amount \( F_s * X_{\text{t},i} \) taking into account the reforming ratio (RR)

\[
S_{H_2,i} = \frac{F_{H_2,i}}{F_s * X_{\text{t},i}} \times \frac{1}{\text{RR}} \times 100
\]

RR describes the theoretical maximum of hydrogen that can be produced from the reactant if all the carbon would be gasified to CO₂.

RR for EG is 5/2:

\[
\begin{align*}
C_2H_6O_2 & \rightarrow 2CO + 3H_2 \quad \text{(optimal reforming)} \\
2CO + & 2H_2O \rightarrow 2CO_2 + 2H_2 \quad \text{(WGS)} \\
C_2H_6O_2 & \rightarrow 2CO_2 + 5H_2 \quad \text{(total reforming in optimal reaction)}
\end{align*}
\]

RR for HYDA is 7/3:

\[
\begin{align*}
C_3H_6O_2 + & H_2O \rightarrow 3CO + 4H_2 \quad \text{(optimal reforming)} \\
3CO + & 3H_2O \rightarrow 3CO_2 + 3H_2 \quad \text{(WGS)} \\
C_3H_6O_2 + & H_2O \rightarrow 3CO_2 + 7H_2 \quad \text{(total reforming in optimal reaction)}
\end{align*}
\]
Selectivities to other products were calculated based on Equation 10. The concentration of the product $x$ ($c_{x,i}^\text{out}$, mol/ml) was multiplied by the averaged flow rate of the corresponding effluent flow rate ($V_i^\text{out}$, mL/min) and the number of carbon atoms in the product $x$ ($N_x^\text{carbon}$). For instance, for ethanol $N_x^\text{carbon} = 2$, and for carbon monoxide $N_x^\text{carbon} = 1$. This sum was then divided by the sum of molar flow rate of the reactant $s$, the number of carbon atoms in $s$ (EG=2, HYDA=3) and the Total Carbon conversion at the given time of reaction.

$$S_{x,i} = \frac{c_{x,i}^\text{out} \cdot V_i^\text{out} \cdot N_x^\text{carbon}}{N_s^\text{2} \cdot 2 \cdot X_{t,i}} \ast 100$$ (10)

The yields of the products (H$_2$ and carbon containing) were calculated by taking into account the Total Carbon conversion at the given time of the reaction. This is shown in Equation 11.

$$Y_{H_2/x,i} = S_i \cdot X_{t,i}$$ (11)

Catalyst efficiency was also compared by calculation of rate of the reaction per available surface area of Pt ($r_{Pt\text{-}m^2}$, μmol/m$^2\text{Pt}$*min, Equation 12). The conversion of the reactant divided by 100 is firstly multiplied by the molar flow rate of the reactant $s$. Followed by dividing the product with the available surface area of platinum ($A_{Pt}$). This was obtained based on chemisorption results.

$$r_{Pt\text{-}m^2} = \frac{(X_t/100) \cdot F_s}{A_{Pt}}$$ (12)

Turnover frequency for the reactant $s$ conversion (TOF$_s$, min$^{-1}$) measures the number of molecules converted per time unit on the sites available for catalysis. The calculation is shown in the equation below (Eq. 13). The conversion of the reactant was firstly multiplied by its molar flow rate. Secondly, the mass of platinum on the catalyst ($m_{Pt\text{-}cat}$) was divided with the molar mass of platinum ($M_{Pt}$, g/mol) and then the product was multiplied by the dispersion of platinum ($D_{Pt}$). Further, the product in the numerator was divided with the product in the denominator.

$$\text{TOF}_s = \frac{X_t + F_s}{(m_{Pt}/M_{Pt}) \cdot D_{Pt}}$$ (13)

Turnover frequency for hydrogen production (TOF$_{H_2}$ min$^{-1}$) was calculated in similar manner. In Equation 14 the produced H$_2$ flowrate ($F_{H_2}$) is divided with the moles of the available sites.

$$\text{TOF}_{H_2} = \frac{F_{H_2}}{m_{Pt\text{-}cat}/M_{Pt} \cdot D_{Pt}}$$ (14)
Weight hourly space velocity (WHSV) describes the grams of reactant fed to the reactor per catalyst mass (gram) per hour.

5 References

Figure 1. Schematic representation of the APR setup used in this study.
Figure 5. Schematic presentation of ATR-IR setup with ATR-IR principle in the bottom.
Original APR setup and improvements

In this section, the original APR setup is described. In Figure S2 the setup that was used for Chapter 4 is shown. After finishing this study, it became clear that for better operation and for more detailed analysis of products improvements were necessary.

The improvements are in indicated in Figure S2 in numbers: 1) larger syringe pump was installed to allow the system to run for longer period without needing to fill the pump during the experiment. 2) N₂ gas line was installed to add a standard gas (10ml/min) for more accurate measurement of feed composition. 3) The sampling vessel was modified to add a glycol cooling (±10 °C) to avoid excess moisture from reaching the GC via the sampling port. 4) Another sampling port was added to the sampling vessel to allow sampling continuously during measurement for determining effluent composition (HPLC). 5) Gas flow meter was upgraded from Brooks SLA-5860S (0-100 ml/min) model to Brooks GF40 (0-280 ml/min) to allow measurement of higher product gas flowrates.

Calculations used in Chapter 4

Carbon to gas conversion was defined as the percentage of carbon in the feed that was transformed to carbon in gaseous products (COₓ, hydrocarbons) and was calculated according to:

\[ X_{C \to \text{Gas}} = \frac{p_{\text{carbon in feed}} - p_{\text{carbon in reactor effluent}}}{p_{\text{carbon in feed}}} \times 100\% \]  
(1)

Selectivity to carbon containing gas phase products (i = COₓ, CH₄ and C₂₅) was calculated according to:

\[ S_i = \frac{p_{\text{carbon in species } i}}{\sum p_{\text{carbon in species } i}} \times 100\% \]  
(2)

Selectivity to hydrogen was defined as the percentage of the maximal theoretical amount of hydrogen that can formed based on the gasified carbon and is expressed as:

\[ S_{H_2} = \frac{p_{\text{H}_2 \text{ produced}}}{p_{\text{carbon in gas phase}}} \times \frac{1}{RR} \times 100\% \]  
(3)
Figure 5.1: Schematic presentation of APR setup before improvements.
Chapter 4
Towards stable catalysts for aqueous phase conversion of ethylene glycol for renewable hydrogen

Aqueous-phase reforming of ethylene glycol over alumina-supported Pt-based catalysts is reported. Pt/γ-Al₂O₃ deactivates irreversibly because the Pt surface area decreases owing to an increasing metal particle size and coverage with boehmite. However, Pt supported on boehmite itself shows stable activity. Surprisingly, the rate of formation of hydrogen per Pt surface atom is significantly higher on boehmite compared to an alumina-supported catalyst. This observation seems correlated to both increased concentration of surface OH-groups as well as to enhanced oxidation of Pt when comparing Pt/γ-Al₂O₃ with Pt/AlO(OH).

1 Introduction

Environmental concerns and energy shortage have driven the modern society to seek for alternative, sustainable energy sources to replace fossil fuels. Waste biomass streams are renewable feed stocks for valorization to fuels [1, 2]. In the case of hydrogen or syngas as the targeted fuel or fuel precursor, respectively, steam reforming is the preferred route [1-4]. Steam reforming (SR) is usually carried out at higher temperatures (>750 °C) as the reaction is strongly endothermic and requires activation of water.

Biobased feed stocks consist typically of organic components dissolved in water. For example, aqueous phase of pyrolysis oil contains up to 20 wt% of oxygenated components [2]. The primary difficulty in gasification via steam reforming of such feedstocks is the energy efficiency of the conversion due to the necessity of vaporizing high amounts of water. Dumesic and co-workers [1] introduced Aqueous Phase Reforming (APR) for production of hydrogen rich gas from dilute aqueous oxygenated feed stocks. In APR water is kept in a liquid state by applying pressure at moderate temperatures (e.g. T=225-450 °C, p=2.9-25 MPa) [1, 5]. Thermodynamics favor formation of hydrogen under these conditions [6], however formation of alkanes e.g., methane, in parallel, lowers hydrogen selectivity. Studies with model oxygenate components typically found in biomass waste streams [1, 7], show that dehydration of the oxygenate leads to hydrocarbon formation. Formation of hydrogen requires, however, break down of the carbon chain to C$_0$, which undergoes oxidation via water to form CO$_2$ and hydrogen.

Thus, in order to achieve a high hydrogen yield, catalysts for APR should be active in C-C bond scission and in WGS reaction (CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$). Pt based catalysts are often reported as they are active for C-C cleavage and at the same time efficient for SR/WGS reactions [8-11]. In mechanistic sequence, activation of water is usually achieved via formation of hydroxyl groups on oxide supports. Hydroxyl groups then react with the “C” residue on the Pt metal to complete SR/WGS reactions [2-4]. Therefore, the catalyst support plays a crucial role and catalysts are thus bi-functional. This bi-functional mechanism requires the active metal sites, such as Pt, to be situated in the close proximity of the support OH-groups [3].

Catalyst stability during APR is a challenging issue. Especially in the case of biobased feed stocks, coke and char formation causes severe problems for both catalysts and reactors. Additionally, harsh hydrothermal conditions during APR shorten catalyst lifetime as result of leaching, sintering of metals and/or the support [5, 12].

In general, development of efficient catalysts requires a thorough understanding of the reaction sequences that take place on the catalyst surface, which can often be achieved via in situ studies. FTIR spectroscopy is a tool for such studies, in particular Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) makes this possible in
liquid phase [13, 14]. However, it is challenging to use this technique at typical reaction conditions for APR [15, 16].

Pt/γ-Al₂O₃ has been reported as a promising catalyst for the APR conversion of bio-wastes to hydrogen.[1, 5, 12] It was shown earlier by ex-situ studies[7, 17] that γ-Al₂O₃ undergoes phase change to boehmite (aluminium oxy-hydroxide (AlO(OH))), when exposed to hot compressed water. Boehmite is the thermodynamically stable form of alumina in aqueous environment at temperatures higher than 150 °C [18], including typical APR conditions. This phase transformation results in a decreased surface area [5, 19], and can have detrimental effects on the catalyst performance due to facilitating growth of metal particles[5] and possible blockage of the metal surface by a newly formed layer of boehmite [7].

In this study, activity and stability of Pt/γ-Al₂O₃ catalyst for APR of ethylene glycol (EG) is investigated. The conversion of γ-Al₂O₃ to boehmite is studied with in-situ ATR-IR spectroscopy in hot compressed water. This phase transformation is accompanied by catalyst deactivation. However, using boehmite as catalyst support results in a remarkably stable catalyst with high H₂ yield. This is probably due to the high concentration of surface-OH-groups [20], which can be beneficial for both SR and WGS reactions since OH-groups are essential for water activation.

2 Experimental

2.1 Catalyst preparation

Pt/γ-Al₂O₃ and Pt/AlO(OH) catalysts were prepared by wet impregnation of γ-Al₂O₃ support (BASF AL-3992) and AlO(OH) support, respectively. Supports were crushed and sieved to particle size 300-600µm. AlO(OH) was prepared by subjecting γ-Al₂O₃ to water at 270 °C and 90 bar for 45 min. H₂PtCl₆•6H₂O (Alfa Aesar) was used as platinum precursor. Alumina support was added to the solution of precursor in water (weight ratio H₂O/alumina=1.8) and water was removed under vacuum at 100°C. Catalysts were subjected to a hydrogen treatment (H₂ 100 ml/min, N₂ 100 ml/min) for 5 hours at 100 °C in order to minimise chlorine from Pt precursor. Finally, the Pt/γ-Al₂O₃ catalyst was calcined at 500 °C and the Pt/AlO(OH) catalyst was calcined at 350 °C for 15 hours under air flow (200 ml/min).

2.2 Catalyst characterization

Platinum loadings on catalysts were measured by X-ray fluorescence (XRF) (Philips, PW 1480). Catalysts surface areas were analysed by applying BET-method (Micrometrics, ASAP 2400). Transmission electron microscopy (TEM) imaging (Philips CM300ST-FEG 300 kV microscope equipped with EDX and EELS) was performed to gain information of the platinum particle size on the supports making weighted average of about 100 particles. Platinum dispersion for fresh Pt/γ-Al₂O₃ was also measured by CO
pulse chemisorption (Micrometrics Chemisorb 2750). Before CO chemisorption catalyst were reduced in hydrogen at 200°C for 1 hour. X-Ray diffraction (XRD) spectra were collected for the boehmite support as well as for the fresh and spent catalysts to determine the phase of the support. XRD spectra were collected between 2θ=10-70° with Bruker 2D Powder diffractometer equipped with Cu Kα1 radiation source.

2.3 Kinetic experiments

Aqueous phase reforming experiments where performed in a continuous flow fixed bed reactor using 5 wt% ethylene glycol in water as a feed. Typical reaction conditions were 270°C, 90 bar and catalyst loading of 1 g. The flowrate of the liquid feed was kept at 2 ml/min. Hydrogen selectivity was calculated based on the converted amount of ethylene glycol to carbon containing molecules in the gaseous product stream defining 100% selectivity as complete conversion of ethylene glycol to exclusively to CO₂ and H₂. Selectivity to carbon containing gaseous products assuming maximal reforming ratio (RR)[1, 7] for EG into H₂/CO₂ is 5/2. Details of calculations are presented in Chapter 3.

Hydrogen formation rate was calculated based on the initial hydrogen production rates (mol/s) per Pt surface atom. The number of Pt surface atoms was calculated from TEM, assuming hemi-spherical particles.

2.4 ATR-IR experiments

ATR-IR spectra were collected using FT-IR spectrometer (Bruker, Tensor 27) equipped with liquid nitrogen cooled MCT detector and ATR-IR Tunnel cell (Axiom) mounted in sample chamber. Every spectrum was recorded with 4 cm⁻¹ resolution averaging 256 scans for background spectra and 128 scans for liquid and gas phase spectra.

An internal reflection element (ZnSe rod, diameter 6.4 mm, length 70 mm) was spray-coated with catalyst and carefully placed inside the tunnel cell using O-rings (Kalrez 7075). The cell was connected to gas or liquid inlet. Pre-treatment of the catalyst layer was done in He (20 ml/min) at 150°C in order to remove any solvent traces used during catalyst immobilization. The sample was oxidized in 40 vol% O₂/He mixture (50 ml/min) at the same temperature and cooled down to room temperature in 50 vol% H₂/He flow (50 ml/min). CO gas phase adsorption was done at room temperature during 1 hour in a 20 vol% CO/He mixture (25 ml/min).

In liquid phase experiments, degassed water was pumped (1 mL/min) into the system until 40 bar by HPLC pump (Dionex P680) and heated to APR temperatures (150-210°C). The catalyst was first heated to 150°C, followed by stepwise further heating with 10 degrees, keeping the sample for 30 minute isothermal at each step. Spectra were recorded in the end of each step.
3 Results

Performance of Pt/γ-Al₂O₃ and Pt/AlO(OH) were tested in APR of ethylene glycol (EG). Figure 1 shows TEM micrographs of the two catalysts as a typical example of particle size distribution. Pt particle size was estimated from weighted average based on ~100 particles. Table 1 shows the characteristics of the catalysts. The fresh Pt/γ-Al₂O₃ has a surface area of 182 m²/g, contains about 1.7 wt% Pt, an average particle size 2.4 nm, with standard deviation of 1.3. For this catalyst CO chemisorption confirmed the Pt particle size of 2.4 nm corresponding to 43% dispersion. Pt/AlO(OH) (fresh) has a lower surface area (36 m²/g), and relatively larger Pt particles of ~ 5.7 nm.

Both catalysts were tested in APR of 5 wt% of EG at 270 °C and 90 bar for 5 hours. As shown in Figure 2, after 5 hours Pt/γ-Al₂O₃ showed loss of activity (up to 20%), while Pt/AlO(OH) maintained stable activity, the small increase in activity during the experiment is within the margin of error.

![Figure 1. TEM images of fresh Pt/AlO(OH) (a) and used Pt/γ-Al₂O₃ (b)](image)

Table 1. Catalyst characterization results.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt loading</th>
<th>BET surface area</th>
<th>Average Pt particle size[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>m²/g</td>
<td>nm</td>
</tr>
<tr>
<td>Pt/γ-Al₂O₃ fresh</td>
<td>1.7</td>
<td>182</td>
<td>2.4±1.3</td>
</tr>
<tr>
<td>Pt/γ-Al₂O₃ used (5 hours)</td>
<td>1.6</td>
<td>33</td>
<td>6.3±1.7</td>
</tr>
<tr>
<td>Pt/AlO(OH) fresh</td>
<td>1.4</td>
<td>36</td>
<td>5.7±1.2</td>
</tr>
<tr>
<td>Pt/AlO(OH) used (5 hours)</td>
<td>1.4</td>
<td>20</td>
<td>5.7±1.2</td>
</tr>
</tbody>
</table>

[a] weighted average and standard deviation based on ~ 100 particles from TEM micrographs.
Figure 2. Conversion of 5 wt% of ethylene glycol over Pt/γ-Al₂O₃ and Pt/AlO(OH) catalysts at 270 °C and 90 bar; the purpose of the lines is to guide the eye.

The stability of Pt/AlO(OH) under APR conditions makes it an interesting support. Table 2 shows details of the performance of the two catalysts. The hydrogen formation rate expressed in mole H₂ per sec per mole surface Pt (Turn over frequency, TOF) was calculated for the first 30 minutes on stream. The number of Pt atoms on the surface was calculated based on the metal-particle-size data as determined by TEM.

In order to determine the reasons for the deactivation, used Pt/γ-Al₂O₃ catalyst was characterized post-mortem. As indicated earlier, since the catalysis for APR is bi-functional, changes with respect to both Pt and γ-Al₂O₃ may be responsible for deactivation.

Figure 3 shows the XRD patterns for the catalysts. The XRD spectrum of fresh Pt/γ-Al₂O₃ is characteristic for γ-Al₂O₃. The spectra of used Pt/γ-Al₂O₃ and both fresh and used Pt/AlO(OH) resembles the structure of boehmite.

Table 2. Comparison of initial rate of formation of H₂, and selectivities to gas phase carbon containing products, APR, EG, 270 °C, 90 bar.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF</th>
<th>CO</th>
<th>CO₂</th>
<th>C₆H₁₂[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol/s*mol_Pt</td>
<td>mol%</td>
<td>mol%</td>
<td>mol%</td>
</tr>
<tr>
<td>Pt/γ-Al₂O₃</td>
<td>1</td>
<td>11</td>
<td>81</td>
<td>9</td>
</tr>
<tr>
<td>Pt/AlO(OH)</td>
<td>5</td>
<td>6</td>
<td>92</td>
<td>2</td>
</tr>
</tbody>
</table>

[a] C₄-C₃ alkanes
Towards stable catalysts in APR of EG

Figure 3. XRD patterns for the catalysts used in the study.

To study the details of the in-situ transition of $\gamma$-Al$_2$O$_3$ into boehmite during APR, an in-situ ATR-IR cell was developed that enables catalyst studies under elevated temperature and pressure up to 210 °C and 40 bars in water. The structure of the ATR-IR cell is presented in Chapter 3. This cell was used for the in-situ study of support stability under conditions approaching practical conditions for APR. Details on the principles of ATR-IR spectroscopy in liquid phase heterogeneous catalysis can be found in the literature[13] and references therein.

Figure 4a shows the ATR-IR absorbance spectrum of boehmite in water at 40 bar and 210 °C. Hydroxyl stretching/bending vibrations (3305, 3125 cm$^{-1}$/ 1060 cm$^{-1}$) corresponding to boehmite can be clearly seen in addition to the typical water bending vibration at 1635 cm$^{-1}$ and hydroxyl stretching between 3200 – 3600 cm$^{-1}$.

ATR-IR spectra were collected in a 5 hour experiment during which temperature was increased stepwise from 150 to 210°C at 40 bar (Figure 4b). The sharp peak at 1060

Figure 4. (a) Typical ATR-IR absorbance spectrum of pure boehmite in water at 40 bar and 210 °C; (b) Integrated area of OH deformation peak (1060 cm$^{-1}$) with time and temperature during catalyst hydrothermal exposure.
cm\(^4\) was integrated to quantify the amount of boehmite present during the experiment (Figure 4b, red circles). It should be noted that the absolute intensities for the three different catalysts cannot be compared quantitatively because of uncertainty about the penetration depth of the evanescent wave in the three samples. Clearly, boehmite is stable in time and at all temperatures. The same experiments were performed for Pt/\(\gamma\)-Al\(_2\)O\(_3\) (blue triangles) and Pt/AlO(OH) (black squares). The Pt/\(\gamma\)-Al\(_2\)O\(_3\) catalyst shows a threefold increase in boehmite formation with time and temperature. It is important to note that phase transformation of \(\gamma\)-Al\(_2\)O\(_3\) takes place with significant rate even at conditions milder than practical APR conditions. A full analysis of the kinetics of boehmite formation under these conditions is outside the scope of this study, and is presented in a follow-up study[14]. The Pt/AlO(OH) sample shows obviously a much higher intensity than Pt/\(\gamma\)-Al\(_2\)O\(_3\) at the end of stepwise experiment. The boehmite intensity for Pt/AlO(OH) increases slightly with time and temperature, indicative of the presence of some \(\gamma\)-Al\(_2\)O\(_3\)\(_3\), which was probably formed by calcining at 350\(^\circ\)C as part of the preparation procedure.

The ATR-IR experiments were also performed on Pt/\(\gamma\)-Al\(_2\)O\(_3\) with 0.2 mol/l ethylene glycol in water (result not shown). This experiment revealed that boehmite formation slowed down in the presence of ethylene glycol in agreement with earlier studies [19].

Before and after the ATR-IR experiment in water, the platinum particles in both catalysts were characterized by CO adsorption on the immobilized layer. The freshly deposited catalyst layer was calcined and reduced as described in the experimental section. After the hydrothermal experiment, the catalyst layer was dried at 150 \(^\circ\)C and cooled in helium to room temperature. In both situations, subsequently, CO gas was introduced in the ATR-IR cell at room temperature. The resulting spectra for Pt/\(\gamma\)-Al\(_2\)O\(_3\) and Pt/AlO(OH) are shown respectively in Figure 5a and b.

![Figure 5. ATR-IR spectra of gas phase room temperature CO adsorbed on (a) fresh and used Pt/\(\gamma\)-Al\(_2\)O\(_3\), (b) fresh and used Pt/AlO(OH). Peaks related to gas phase CO molecule were subtracted.](image-url)
CO adsorbed on Pt/γ-Al₂O₃ shows a broad peak with a maximum at 2072 cm⁻¹ and a shoulder at 2112 cm⁻¹ (Figure 5a). The peak at 2072 cm⁻¹ can be ascribed to linearly bound CO on Pt [13, 16, 21]. The peak at 2112 cm⁻¹, is assigned to partially oxidized Pt [21, 22]. After hydrothermal treatment, the 2072 cm⁻¹ band strongly decreased in intensity and shifted slightly to 2069 cm⁻¹, and the band at 2112 cm⁻¹ became more prominent. The clear decrease of accessible platinum surface area as observed in Figure 5a is in good agreement with increasing metal particle size as reported in Table 1.

Figure 5b shows CO adsorbed on fresh and used Pt/AlO(OH) catalyst. Again, the fresh Pt/AlO(OH) shows a broad peak, but this time at 2112 cm⁻¹, indicative of partially oxidized platinum. After hydrothermal exposure this band almost doubled in intensity and a shoulder at 2067 cm⁻¹ became apparent. Clearly, platinum supported on boehmite is mainly in partially oxidized condition both after reduction of the fresh catalyst as well as after being exposed to hydrothermal conditions. The increased intensity of the 2112 cm⁻¹ band might point to a redistribution of platinum particles during the high pressure, high temperature treatment. However, this is speculative at the moment.

4 Discussion

Results shown in Table 1 indicate that Pt content in the catalysts did not change on use, indicating that no leaching and loss of Pt occurred during the reaction under APR conditions. In the case of Pt/γ-Al₂O₃, the average Pt particles sizes increased from 2.4 to 6.3 nm as determined from the TEM images, indicating sintering of the metal particles. For this catalyst, parallel to the loss of activity, also the support surface area reduced drastically on use at APR conditions (Table 1).

Based on the fact that under hydrothermal conditions γ-Al₂O₃ undergoes phase change to AlO(OH) support [7, 17] it is not surprising that the surface area of Pt/γ-Al₂O₃ reaches that of Pt/AlO(OH) (Table 1). Moreover, AlO(OH) was prepared by hydrothermal treatment of γ-Al₂O₃ at conditions similar to APR reaction conditions (see experimental section). Thus, during the APR experiment, γ-Al₂O₃ is unstable and susceptible to phase change, while boehmite is stable.

However, it has been shown earlier that during APR of ethylene glycol [7], phase transformation of γ-Al₂O₃ by hydrolysis leads to dissolution and subsequent re-precipitation of boehmite on Pt metal particles. This was attributed to the formation of acetic acid during APR of ethylene glycol, which was confirmed by separate acetic acid APR experiments [7]. This leads to encapsulation of platinum (Figure 7) making the Pt particles not accessible for reactants. Lower amount of CO adsorbed on the used Pt/γ-Al₂O₃ catalyst in our studies (Figure 6a) is also in line with this observation.

Thus, the deactivation of Pt/γ-Al₂O₃ catalyst during APR of ethylene glycol has contributions from both metal sintering and coverage of the metal surface due to the phase change of the support. Loss of surface area as well as the hydroxylation of the
surface may both be responsible for the Pt particle growth that is observed. In contrast, Pt/AlO(OH) remains active despite a small decrease in the BET surface area (Table 1); apparently this does not cause any metal sintering and metal coverage.

Remarkably, in addition to being stable, Pt/AlO(OH) shows tremendous improvement in the rate of formation of hydrogen (Table 2) during APR of ethylene glycol. In contrast, the activity data in Figure 2 suggest that Pt/AlO(OH) is less active than Pt/Al₂O₃; it should be noted that the Pt loading of the γ-alumina supported catalyst is higher (1.7 versus 1.4 wt%) and that the initial metal particle size is much smaller on γ-alumina. Even more important is the fact that the selectivity to alkanes is much lower for Pt/AlO(OH), resulting in significant higher H₂ yield.

Further, the selectivity to CO₂ increased as well, with a corresponding decrease in CO, which is indicative for improved WGS activity. Obviously, all this contributes to an improved hydrogen production rate for Pt/AlO(OH).

In bi-functional catalysis involving water, e.g., steam reforming and WGS reactions, activation of water can be the critical step. Water activation on oxide supports is proposed to occur via formation of hydroxyl groups depending on the redox properties the oxide[23, 24]. In our experiments we see that AlO(OH) support enhances the rate of hydrogen formation. In order to understand the difference between AlO(OH) and γ-Al₂O₃ ATR-IR spectra of the two catalysts in gas phase was recorded (Figure 7). The concentration of hydroxyl groups is significantly higher for Pt/AlO(OH). Furthermore, the IR data of adsorbed CO (Figure 4) clearly indicate that Pt is more easily oxidized when supported on AlO(OH). We suggest that these three phenomena are correlated, although we are at this time not in a position to decide on causal relationships. OH groups may be directly relevant by providing a path for water activation. On the other hand, OH groups might be responsible for inducing charge on Pt, whereas charged Pt may enhance the reaction pathway to H₂. Alternatively, it may
be suggested that water is able to oxidize Pt under these conditions, in agreement with
suggestions by Zhang et al [25] based on an XPS study.

In general, based on stability it is suggested that boehmite phase is suited to low
temperature aqueous phase reforming, while γ-Al₂O₃ is more suitable for high
temperature steam reforming catalysis. Design of an active, stable and selective catalyst
based on boehmite is promising.

5 Conclusions

ATR-IR demonstrated real-time conversion of γ-Al₂O₃ to boehmite under
conditions (210 °C and 40 bars) even somewhat milder than practical conditions for APR
of ethylene glycol (typically 270 °C). This is in agreement with catalyst deactivation, as
contributed to Pt sintering as well as blocking the Pt surface with boehmite.

The boehmite phase, once formed, is stable at APR conditions. Boehmite is an
efficient support for Pt based catalysts for APR of ethylene glycol, exhibiting excellent
activity for hydrogen formation. This may be caused by both the extensively
hydroxylated boehmite surface, possibly favouring the bi-functional reforming
mechanism involving adsorbed carbonaceous species on Pt and water activation via
hydroxyl groups on the support, as well as by enhancing oxidation of Pt.

6 References

Chapter 5

Development of stable catalyst supports for aqueous phase reforming of oxygenates – Studies with hydroxyacetone

Aqueous-phase reforming (APR) is an attractive process to generate hydrogen from biomass waste streams. Dilute (up to 20% organics) feedstocks can be utilized with this process in hot compressed water (e.g. 225 °C/35 bar) using a catalyst. Unfortunately, under these conditions and due to the reactive feedstocks/products, catalyst stability is often challenged, e.g. by changes in the catalyst structure or by coke/char formation during the reaction. We explored performance of three catalysts, Pt/C, Pt/AlO(OH) and Pt/ZrO₂ in APR, with a challenging model component i.e., hydroxyacetone (2.4 wt% in water), at 225 °C, 35 bar. Pt/C catalyst showed stable performance and excellent Carbon to Gas Conversion compared to AlO(OH) and ZrO₂ supported Pt catalyst during 6 hours on stream. Stable performance was achieved due to minimized conversion of reactant to the liquid phase by-products. Furthermore, higher H₂ yield with the carbon supported catalyst was achieved as hydrogen consuming by-products, such as alcohols, were suppressed. Over oxide supported catalysts side reactions in the aqueous phase consumed hydrogen and also resulted in the formation of coke/char leading to catalyst deactivation.

Chapter 5

1 Introduction

Waste water streams from, e.g., food industries or bio-refineries have aqueous effluents that contain dissolved organics, typically in the range of 5-20 wt %. Processing these waste streams to value added products such syngas (CO + H₂) or hydrogen is energy intensive with the conventional reforming processes, which operate at higher temperatures (>750 °C) and intermediate pressures (< 25 bar) [1], due to the need to vaporize large amounts of water. Dumesic and co-workers tackled this problem by developing the “Aqueous Phase Reforming” (APR) process in which water is kept in the liquid phase by applying elevated pressures [2-4]. The concept was further demonstrated for hot water reforming of diluted oxygenate feeds at mild temperatures in pressurized liquid water (225 – 265 °C, 29 – 56 bar) over supported metal catalysts [5-8]. For example, typical temperatures for fundamental APR studies of model components (e.g. ethylene glycol, methanol and sorbitol) were usually in the temperature range of 200-265 °C[3, 9]. The purpose of these studies has been to identify pathways that lead to hydrogen and prevent formation of by-products. The key challenge for chemistry and catalysis during APR is to achieve C-C bond cleavage, to result in C1 specie which on further oxidation by water yields carbon oxides and hydrogen.

By-product selectivities and catalyst deactivation are key issues that need to be addressed for industrial exploitation of this process [5]. In terms of products, complete conversion of feed/reactant oxygenates to CO₂ maximizes hydrogen yields (e.g., Eqn. 1). Formation of alkanes, especially methane which is thermodynamically favorable under APR conditions, lower hydrogen yields and should be minimized. Further, also liquid products such as acids, aldehydes, alcohols etc., when formed remain in the aqueous phase and cause incomplete conversion of the feed reactant. Some of these products are unstable and via secondary reactions, such as condensation, polymerization, form coke/char/tar and destabilize catalysts.

\[ \text{C}_3\text{H}_6\text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 3 \text{CO}_2 + 7\text{H}_2 \quad (1) \]

Other catalyst stability issues in hot compressed water (sub- or super-critical) are mainly related to sintering or loss of catalytic material via leaching of the supported metal particles, e.g. Pt, [10] or dissolution of metal oxide supports, e.g. Al₂O₃, TiO₂ and ZrO₂ [11, 12]. Several authors have reported on the hydrothermal instability of catalysts during APR of model oxygenates [13-16]. To summarize, the challenge to make sub- or supercritical water reforming of biomass derived waste streams requires design of catalysts that (i) show high stability in hot compressed water and are stable against impurities or poisons, such as tars, (ii) minimize coke/char formation, (iii) are able to convert concentrated feed streams (typically >15 wt %) under industrially relevant residence times, i.e., have high catalytic activity, and (iv) maximise H₂ yields. A fundamental understanding of the reforming pathways and deactivation mechanisms is mandatory for the development of such catalysts.
Catalyst deactivation due to coke/char formation is still a major issue in the successful design of efficient catalysts. A variety of reports have addressed the issue of coke/char formation during APR of oxygenated feedstocks [8, 17, 18]. Acetic acid is one of the products observed in significant amounts during APR conversion of most oxygenates due to oxidation of the feed molecule by water [7, 15, 17, 19, 20]. It is also one of the most problem components during steam reforming [21-25] with regards to coke formation. Acetic acid, if not reformed efficiently, undergoes ketonization to acetone. Acetone is a precursor to coke formation via forming condensation intermediates such as di-acetone alcohol, ketene etc. and cause severe catalyst deactivation [17, 21, 24]. Olefins, aldehydes, formed during APR. also cause coke formation by polymerization, condensation, respectively [26, 27].

Supported Pt catalysts have often been reported as promising for APR of aqueous phase oxygenates [5-8]. In this case, a definite role for the oxide support is suggested in order to activate water via formation of hydroxyl groups, e.g., γ-Al₂O₃ or undergoing redox changes, e.g., CeO₂ [28]. Thus, the Pt supported catalysts are often referred to as bifunctional, i.e. having a role for both the metal and the support. In the case of conventional Nickel based catalysts, Ni metal itself also plays the role for water activation via nickel-nickel oxide red-ox cycle [1]. Thus most commercial based Ni catalysts are supported on inert α-Al₂O₃.[1]. High surface area oxide supports, e.g., γ-Al₂O₃, show acidity, Bronsted acidity due to presence of hydroxyl groups, and Lewis acidity is caused by anion vacancy and thus unsaturated cation sites (Al³⁺). Unfortunately, acid centres on the supports, both Lewis and Bronsted sites, play significant roles in catalyzing coke/char formation [29]. Thus, in the development of an efficient Pt catalyst, the choice of support is critical.

The target of this work is to develop an efficient and stable catalyst based on Pt for APR of aqueous wastes. In order to achieve/model this, we have chosen a problem component such as hydroxacetone (HYDA) for the following reasons, (i) it is present in appreciable amounts in the aqueous phase of pyrolysis oil, a waste-by-productstream in the production of fossil compatible bio-fuels from lignocellulosic biomass, (ii) it is one of the problem components that cause coke formation as discussed above and (iii) very little is reported on catalytic APR conversion of HYDA. In order to establish the role of acidity of the catalyst on selectivity and stability, Pt supported on materials with varying acidity, e.g., Boehmite (AlO(OH)), Zirconia (ZrO₂) and Mesoporous Carbon (C) were studied. Catalyst characteristics and their relation to reaction product selectivities and stability are discussed.

2 Experimental

2.1 Catalyst preparation

ZrO₂ support (Monoclinic, RC100, Gimex Technisch Keramik B.V., NL) was obtained as powder and was first pelletized, crushed and sieved to particle size range
300-600µm. AlO(OH) support was prepared from crushed γ-Al₂O₃ pellets that were sieved to 300-600µm (Alfa Aesar) and subjected to hot compressed water at 200°C in an autoclave (14 bar) for 10 hours. The formation of Boehmite phase was confirmed by XRD. Sibunit mesoporous carbon support was provided by Boreskov Institute of Catalysis with grain size of 250-500µm. All Pt catalysts, 1.2 wt% Pt/ZrO₂, 1.2 wt% Pt/AlO(OH), and 1.2 wt% Pt/C (Sibunit) were prepared by wet impregnation, using H₂PtCl₆•6H₂O (Alfa Aesar) as platinum precursor. The supports were added to the solution of precursor in water (weight ratio water/support=1.8) and water was removed under vacuum at 100°C. Catalysts were reduced with hydrogen (H₂ 100 mL/min mixed with N₂ 100 ml/min) for 5 hours at 100°C in order to minimize the amount of remaining chlorine, originating from Pt precursor. Finally, the Pt/ZrO₂ and Pt/AlO(OH) catalysts were heated at 300 °C in air (flow rate 200 ml/min) for 15 hours and the Pt/C catalyst was treated at 300°C for 15 hours in N₂ (flow rate 200 ml/min). Catalysts were reduced in-situ with hydrogen present under APR conditions prior start of the experiment.

2.2 Catalyst characterization

Fresh and used catalysts were characterized by XRF, H₂ pulse chemisorption, XRD and TEM imaging. The acidity of the oxide supported catalysts were measured by pyridine FT-IR and NH₃ TPD. The spent oxide supported catalysts and supports were characterized by TPO and elemental analysis. Carbon and Boehmite were characterized by PZC analysis. The details of the characterization techniques are discussed in Chapter 3.

2.3 Catalyst testing

Details of the experimental procedure, analysis of products and definitions are explained in Chapter 3. The experiments carried out in this Chapter were done with 2.4 wt% hydroxyacetone (HYDA) (Alfa Aesar, 95%) solution in water as feed over 1 gram of catalyst at 225 °C and 35 bar. The feed composition is shown in Table 1. Pt/ZrO₂ and Pt/C catalyst were tested with feed flow rate of 2ml/min (WHSV 3 h⁻¹). Pt/AlO(OH) was tested with 1ml/min flow rate (WHSV 1.5 h⁻¹) in order to obtain similar conversion as with the other two catalysts. The pressure drop over the catalyst bed was at the maximum 3-5 bars, as observed with the oxide supported catalysts, probably caused by the presence of a significant fraction of fine particles. Conversion of HYDA without any catalyst (hereafter noted as “Thermal”) in the reactor was tested by filling the reactor with inert SiC with similar bed volume of the catalyst bed and by using the same flowrates. Activity of blank supports were also tested applying the same flowrates as for the corresponding catalysts.
Table 1. Feed composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol%</td>
</tr>
<tr>
<td>Hydroxyacetone</td>
<td>96.10</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.50</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>0.50</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0.50</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>1.30</td>
</tr>
</tbody>
</table>

3 Results

3.1 Characterization of catalysts

Characterization results of catalysts studied are shown in Table 2. The Pt loadings of all three catalysts, as prepared, are similar. TEM images gave average Pt particle size for all catalysts which is similar to Pt size measured by hydrogen chemisorption. Particle size distributions from TEM imaging are shown in Figures 1-3 for the catalysts. Pt particles size for fresh Pt/ZrO2 catalyst were not calculated by TEM since the resolution between Pt and ZrO2 was too low to determine Pt size accurately. Pt dispersions and metal areas calculated based on the hydrogen chemisorption results are also shown in Table 2.

Table 2. Characteristics of the catalysts studied.

<table>
<thead>
<tr>
<th>Fresh catalyst</th>
<th>Pt loading</th>
<th>BET</th>
<th>Pt size TEM</th>
<th>Pt size Chemisorption</th>
<th>Pt dispersion*</th>
<th>Av*</th>
<th>PZC*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>m²/g</td>
<td>nm</td>
<td>nm</td>
<td>%</td>
<td>m²/gmetal</td>
<td></td>
</tr>
<tr>
<td>Pt/C</td>
<td>1.2</td>
<td>257</td>
<td>2.9</td>
<td>3.7</td>
<td>31</td>
<td>76</td>
<td>2</td>
</tr>
<tr>
<td>Pt/AlO(OH)</td>
<td>1.2</td>
<td>41</td>
<td>5.1</td>
<td>4.9</td>
<td>23</td>
<td>58</td>
<td>8</td>
</tr>
<tr>
<td>Pt/ZrO2</td>
<td>1.2</td>
<td>94</td>
<td>-</td>
<td>1.8</td>
<td>64</td>
<td>159</td>
<td>-</td>
</tr>
</tbody>
</table>

*Calculated from H₂ chemisorption data
*Measured for the catalyst support only
Figure 1. Pt size distributions of fresh and spent Pt/C.

Figure 2. Pt size distributions of fresh and spent Pt/AlO(OH).

Figure 3. Pt size distribution of spent Pt/ZrO$_2$.

78
Table 3. Total Carbon Conversion ($X_c$), Carbon to Gas Conversion ($X_{C2G}$), Carbon to Liquid Conversion ($X_{L0}$), coke amount on tested materials and carbon balance (CB) during APR of hydroxyacetone over the catalysts and supports at first 30 minutes of reaction and during thermal experiment at 225°C/35 bar.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$X_c$</th>
<th>$X_{C2G}$</th>
<th>$X_{L0}$</th>
<th>Coke</th>
<th>CB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>wt%</td>
<td>%</td>
</tr>
<tr>
<td>Pt/C</td>
<td>52</td>
<td>39</td>
<td>12</td>
<td>n.a.</td>
<td>96</td>
</tr>
<tr>
<td>Pt/Al(OH)</td>
<td>58</td>
<td>44</td>
<td>18</td>
<td>1</td>
<td>98</td>
</tr>
<tr>
<td>Pt/ZrO$_2$</td>
<td>57</td>
<td>18</td>
<td>36</td>
<td>4</td>
<td>88</td>
</tr>
<tr>
<td>Carbon</td>
<td>8</td>
<td>3</td>
<td>7</td>
<td>n.a.</td>
<td>93</td>
</tr>
<tr>
<td>Al(OH)</td>
<td>21</td>
<td>3</td>
<td>17</td>
<td>1</td>
<td>96</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>47</td>
<td>12</td>
<td>43</td>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>Thermal (3 h$^{-1}$)</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>n.a.</td>
<td>99</td>
</tr>
<tr>
<td>Thermal (1.5 h$^{-1}$)</td>
<td>10</td>
<td>2</td>
<td>7</td>
<td>n.a.</td>
<td>96</td>
</tr>
</tbody>
</table>

n.a.; not available, carbon balance based on the rest of the products.

In the thermal experiments (Table 3) the gasification activity was low. Change in Space velocities did not influence the gasification (APR) activity. It mainly affected conversion of HYDA in the liquid phase. They were however low. In the case of only supports, higher conversions were observed, but HYDA conversion was mostly towards liquid phase products, thus incomplete APR and formation of intermediate products. The role of supports in the formation of these products and their subsequent influence on the performance of the catalysts, mainly stability, will be discussed later on. In the presence of Pt, much higher conversions (>50 mol%) and mainly gasification activities were observed. Observing the highest amounts of coke as well as liquid phase products formed, ZrO$_2$ seems to be the least suitable support in this situation. Higher amount of coke formation ZrO$_2$ samples also is the reason for the offset in carbon balance. Even though coke deposited on the catalyst was included in the mass balance calculations quantifiable, homogeneous coke (humsins type materials) formed in the liquid phase were not and could not be accounted for.

Desired products in the gas phase are CO$_2$ and hydrogen, expected to form via APR and WGS reactions, see Equations 2 and 3.

$$C_3H_6O_2 + H_2O \rightarrow 3CO + 4H_2$$  \hspace{1cm} (2)

$$CO + H_2O \rightarrow CO_2 + H_2$$  \hspace{1cm} (3)

Typical products observed in the gas phase are carbon oxides, hydrogen, and lower alkanes including methane. Figure 4 shows gas phase product yields obtained over the three catalysts. Hydrogen yields were in the order Pt/Al(OH) > Pt/C >> Pt/ZrO$_2$. In the case of Pt/C highest amount of CO was observed indicating lower WGS
activity. Further, it can be seen that methane was the majority component among the alkanes. High amounts of methane were produced except for Pt/ZrO₂.

Intrinsic rates for Carbon to Gas Conversion and hydrogen formation (TOF, min⁻¹) are also shown in Table 4. The rate for Carbon to Gas Conversion decreased in the order Pt/C > Pt/AlO(OH) > Pt/ZrO₂. TOF for H₂ was similar for Pt/AlO(OH) and Pt/C but for the Pt/ZrO₂ catalyst calculated TOF was very small. Considering that the Total Carbon Conversion of HYDA was high (57%, Table 3) this cannot be due to catalyst deactivation but must be due to hydrogen consumed internally. This will be discussed later on. Thus, the carbon supported catalyst performed the best for gasification as well as hydrogen production, whereas the Pt/ZrO₂ suffered from both accounts. But for the lower WGS activity, Pt/C shows the best promise.

In addition to gas phase products, appreciable amounts of products were also seen in the liquid/aqueous phase. As seen earlier (Table 3) Carbon to Liquid Conversion were lower (12% and 18%) for Pt/C and Pt/AlO(OH), respectively but much higher (36%) for Pt/ZrO₂. In the absence of catalysts conversions to liquid phase products were minimal (Table 3). Observed yields to identified liquid phase products are shown in Figure 5. The main products were C₂-C₃ alcohols, C₄-C₆ carboxylic acids and C₆ ketone. Considering that HYDA is a C₃ oxygenate, the product pattern indicates that a certain amount C-C bond cleavage as well as C-C coupling occurred over the catalysts. Further, it is important to realize that alcohols are products of hydrogenation. Interestingly, over Pt/ZrO₂ highest amount of alcohols were observed.

Over Pt/C, acetic acid, acetone, 1,2-Propane diol (1,2-PDO) and hydroxy propionic acid (Lactic acid, LA) were the main products. Over Pt/AlO(OH), PDO was the main product. Acetic acid, ethanol and acetone were also formed, but to lesser extents than over Pt/C.
Table 4. TOF for Carbon to Gas Conversion and for H₂ formation over the studied catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon to gas</td>
<td>H₂</td>
</tr>
<tr>
<td></td>
<td>min⁻¹</td>
<td>min⁻¹</td>
</tr>
<tr>
<td>Pt/C</td>
<td>41</td>
<td>28</td>
</tr>
<tr>
<td>Pt/AIO(OH)</td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

In order to understand the role of supports in the formation of aqueous phase intermediates, APR of HYDA was also carried out in the absence of catalysts and on bare supports. Observed yields in these cases are shown in Figure 6. It should be noted that the conversion levels were different and the information is only used to compare products formed over the three supports with thermal and catalyzed reactions, qualitatively.

The type of products formed over the supports were similar to those formed over the catalysts, namely, C₂-C₅ alcohols, C₂-C₄ carboxylic acids and C₃ ketone. Table 3 shows that Carbon support gave the lowest amount of liquid phase products (~7%). The inertness of carbon in the conversion of HYDA can be seen in the product yields, they were similar to thermal conversion. Amount of liquid phase products was the highest for ZrO₂ (~43 %) and in between for AIO(OH) (18 %), as shown in Table 3. Further, it is remarkable to note that the amounts of liquid phase products were very high for both Pt/ZrO₂ and ZrO₂ (~43%, see Table 3). Interestingly, 1,2-PDO formation was relatively

Figure 5. Yields to liquid products over the catalysts in APR of 2.4wt% HYDA at 225 °C/35 bar.
high over ZrO$_2$ (4.5%) compared to Carbon and AIO(OH). Over ZrO$_2$ and to a lesser extent over AIO(OH), unidentified products with long retention times were observed in HPLC analysis. The reactor effluent was colored bright yellow over ZrO$_2$ and after a while deposition of humins were observed in the liquid. Over AIO(OH), ethanol and lactic acid were the main products. The presence of liquid phase oxygenates, similar to those formed over catalysts indicate a significant role for the support in the chemistry of HYDA conversion.

### 3.2 TOS performance and catalyst stability

All catalysts and support materials were tested in APR of HYDA. Thermal conversion at the same space velocity (WHSV 3 h$^{-1}$) was 4% and Carbon to Gas conversion was 1%. Figure 7 shows the Total Carbon Conversion and Figure 8 the Carbon to Gas Conversion for all three catalysts as a function of time. The initial HYDA conversions were kept similar, i.e., between 51% and 57% by varying the WHSV. It can be seen from the figures that Pt/C maintained steady activity over a period of 360 min. Both Pt/AIO(OH) and Pt/ZrO$_2$ deactivated in this time period with more than 30 % of the initial activity lost.

As we discussed earlier, both ZrO$_2$ and AIO(OH) caused formation of large amounts of oxygenates in the liquid phase. In order to understand the role, if any, of these intermediates on catalyst stability, HYDA conversion during APR of over the bare supports (Pt absent) is shown in Figure 9. It is seen that both Carbon and AIO(OH) (<20%). ZrO$_2$ showed high initial activity (47%), almost similar to that of Pt/ZrO$_2$ but deactivated with time (Fig 9).
Considering the factors (i) Carbon to Gas Conversion, (ii) hydrogen yields and (iii) stability with time, Pt/C is the most efficient and promising for the APR of HYDA. In the following section, these aspects are discussed in relation to characteristics of the catalysts and the chemistry that takes place during the conversion so that a proposal for the development of an efficient catalyst can be made.

![Figure 7. Total conversion of 2.4wt% of HYDA over the catalysts at 225 °C/35 bar.](image)

![Figure 8. Carbon to Gas Conversion over the catalysts during APR of 2.4wt% HYDA at 225 °C/35 bar. WHSV for Pt/C and Pt/ZrO₂ was 3h⁻¹ and for Pt/AlO(OH) WHSV was 1.5h⁻¹.](image)
3.3 Characteristics of the spent catalysts

Properties of the catalysts after the APR runs were analyzed to understand the observed performance. Details are given in Table 5. Pt loadings of the spent catalysts were similar to fresh ones thus no leaching was concluded. No significant changes in the BET surface area of the Pt/AlO(OH) and Pt/ZrO₂ catalyst were seen. The Pt/C catalyst lost surface area during APR. This is most likely due to filling or blocking of micro-pores during the reaction. In agreement, in the pore size distribution analysis, micro-pores were not observed for the used Pt/C catalyst (not shown). Pt/C catalyst after use showed Pt size similar to fresh catalyst from TEM results. However, chemisorption showed a slight increase of particle size after use. XPS was performed to rule out the effect of contaminants on the used catalyst on hydrogen chemisorption results. Results showed presence of iron on the spent catalyst (probably leached out from the stainless steel reactor walls) which could cause the observation. In the case of Pt/AlO(OH) and Pt/ZrO₂ catalysts both hydrogen chemisorption data and TEM imaging showed changes in Pt sizes and available Pt metal surface areas after use. The Pt surface area of Pt/AlO(OH) catalyst decreased significantly during APR, from 58 to 19 m²/g. Remarkably, the Pt surface area was completely recovered (Pt/AlO(OH)-reg) by oxidizing the sample suggesting that physical blockage by coke deposition was the main cause of the observed metal surface area loss during APR. Similar results were obtained for Pt/ZrO₂. The surface area of Pt decreased from 159 to 49 m²/g. The oxidation treatment allowed only partial recovery of the Pt surface area, i.e., to 71 m²/g. This indicates that sintering of Pt metal particles also played a role. TEM analysis confirms this (see Table 5). The size distributions for the catalysts were shown in Figures 1-3.
Table 5. Characteristics of the spent catalysts.

<table>
<thead>
<tr>
<th>Spent catalysts</th>
<th>Pt loading</th>
<th>BET</th>
<th>Pt size TEM</th>
<th>Pt size Chemisorption</th>
<th>Pt dispersion*</th>
<th>A_Pt*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>m²/g</td>
<td>nm</td>
<td>nm</td>
<td>%</td>
<td>m²/g metal</td>
</tr>
<tr>
<td>Pt/C</td>
<td>1.1</td>
<td>171</td>
<td>3.0</td>
<td>2.9*</td>
<td>40*</td>
<td>99*</td>
</tr>
<tr>
<td>Pt/AlO(OH)</td>
<td>1.3</td>
<td>39</td>
<td>4.6</td>
<td>17.2</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>1.2</td>
<td>93</td>
<td>2.8</td>
<td>5.7</td>
<td>20</td>
<td>49</td>
</tr>
<tr>
<td>Pt/AlO(OH) - reg^</td>
<td>-</td>
<td>-</td>
<td>4.1</td>
<td>4.4</td>
<td>26</td>
<td>64</td>
</tr>
<tr>
<td>Pt/ZrO₂ - reg^</td>
<td>-</td>
<td>-</td>
<td>3.1</td>
<td>3.9</td>
<td>29</td>
<td>71</td>
</tr>
</tbody>
</table>

*Calculated from H₂ chemisorption data
*XPS showed presence of Fe, this could cause the observed increase in Pt size/dispersion
^ reg: regenerated, details see Chapter 3.

3.3.1 Coke deposition on catalysts

It is seen from the results above that coke deposition was an issue in the case of the oxide supported catalysts. It is not possible to determine coke deposition on Pt/C catalyst, however, the catalyst was stable and the carbon balance excellent, indirectly indicating absence of significant coke deposits. In order to estimate the carbon deposits over the oxide supported catalysts, TPO and C-analyses were performed.

![Figure 10. TPO profiles of the spent oxide supported catalysts and the supports after APR. Signals for AlO(OH) and Pt/AlO(OH) have been multiplied by 3 in order to illustrate the peak shapes clearly.](image-url)
Table 6. Measured carbon content (wt%) of the spent oxide supported catalysts and supports.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C analysis</th>
<th>TPO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>wt%</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>3.94±0.06</td>
<td>3.58±0.03</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>4.55±0.07</td>
<td>5.58±0.05</td>
</tr>
<tr>
<td>Pt/AIO(OH)</td>
<td>0.81±0.01</td>
<td>1.22±0.01</td>
</tr>
<tr>
<td>AlO(OH)</td>
<td>0.83±0.00</td>
<td>1.52±0.07</td>
</tr>
<tr>
<td>PtZrO₂ - reg</td>
<td>0.37±0.01</td>
<td>-</td>
</tr>
<tr>
<td>Pt/AIO(OH) - reg</td>
<td>0.30±0.00</td>
<td>-</td>
</tr>
</tbody>
</table>

Error margin is deviation from average based on 3 measurements.

TPO results of spent catalysts and supports are shown in Figure 10. Pt/ZrO₂ and ZrO₂ showed one peak each at 299 and 213 °C, respectively. Pt/AIO(OH) and AlO(OH) showed less reactive coke formation, which oxidized at higher temperatures. Two peaks could be observed for both samples, i.e. at 350°C and 442°C for Pt/AIO(OH) and at 369°C and 459°C for AlO(OH). The carbon contents, calculated from the integrated peak areas in Figure 10, as well as from C-analysis data are shown in Table 6. It can be seen that Pt/ZrO₂ had approximately 3 times more coke deposits than Pt/AIO(OH). Even on bare supports, ZrO₂ formed more coke than on AlO(OH). Coke amount normalized to BET surface area (mg/m²) also showed the highest amount of coke over zirconia.

4 Discussion

4.1 Reaction pathways in APR of hydroxyacetone

APR of HYDA is only scarcely described in literature. At the conditions of APR, a variety of reaction pathways are possible. We have therefore constructed a reaction network based on conversion of HYDA and similar molecules reported in literature [9, 17, 20, 23-25, 30-40]. Scheme 1 illustrates seven different reaction pathways that can occur during APR of HYDA. These include, C-C cleavage, water reforming of the resulting C1 species, and water gas shift reactions in addition to chemical changes HYDA undergoes via dehydrogenation/hydrogenation, hydration/dehydration, rearrangement and condensation reactions. In the following sections, the routes showed in Scheme1 are discussed in detail to prepare a basis for the observed, activity, selectivity and stability of the catalysts.

C-C cleavage and dehydrogenation, reforming and WGS are the most preferred/desired pathways for an APR catalyst to maximize hydrogen production. Dehydrogenation is generally considered as the first step towards hydrogen [9].
Dehydrogenation of HYDA creates pyruvaldehyde (route 1 in the scheme). From this intermediate the preferred next step is dissociative adsorption via C-C cleavage to smaller adsorbed species on the metal (route 1a), such as *CH₃, and *C=OCH₃ and *CO; the symbol where * indicates adsorbed species. These adsorbed species can be converted to H₂ and CO₂ via reforming by water and Water-Gas Shift (WGS). Water reforming of the surface species (Highlighted box A) competes with hydrogenation to from methane and ethanol (route 1d and 1e) [17]. Methanation (Eq. 4, 5) and FT (Eq. 6) from CO₂ + H₂ mixtures can give methane and higher hydrocarbons. APR conditions are favourable (low T, high pressure) for these.

\[
\begin{align*}
\text{CO} + 3 \text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (4) \\
\text{CO}_2 + 4 \text{H}_2 & \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad (5) \\
(2n + 1)\text{H}_2 + n \text{CO} & \rightarrow \text{C}_n\text{H}_{(2n+2)} + n \text{H}_2\text{O} \quad (6)
\end{align*}
\]

Further, from pyruvaldehyde via α-dicarbonyl cleavage and hydrolysis (route 1b) results in acetic acid plus formaldehyde [30].

Instead of the above discussed first dehydrogenation to pyruvaldehyde, HYDA can also directly adsorb, dissociatively, including C-C cleavage via route 2. This would lead to a similarly adsorbed species compared to route 1+1a, but now H-rich species, i.e. *CH₂OH and *COCH₃ (highlighted box B). Further hydrogenation leads to ethanol/methanol (route 2a). Ethanol has been identified as of key intermediate in APR of polyols to form methane [17, 31]. Ethanol can also be reformed to methanol, CO and H₂ (not shown in the scheme). Furthermore, methanol is also a key intermediate to methane and the preference of the catalyst towards methane is determined by the hydrogenation activity of the catalyst [17]. As shown in Scheme 1, ethanol and methane can be formed via most of the other routes that require C-C cleavage and hydrogenation of higher alcohols (routes 4a and 4c). In addition to ethanol and methanol, methane is also a by-product of acetic acid decomposition/reforming (route 1f). In acetic acid reforming the first step is deprotonation of CH₃COOH to CH₃COO that adsorbs on the catalyst surface as a carboxylate. C-C cleavage leads to decarboxylation releasing CO₂. The remaining *CH₃ on the surface can recombine with H to form methane [32].

In presence of water, C-C cleavage of pyruvaldehyde competes with hydrolysis to form lactic acid (route 1f) [33-35]. Lactic acid can further condensate to C₅ products or can thermally decompose to methane and CO₂ via acetic acid and formic acid formation [36]. These are not shown in the scheme to avoid complexity.

Enolization of HYDA can occur in water [37]. In route 3 the two tautomers are shown and the aldehyde can also be hydrated to lactic acid (route 3b). According to Yaylayan et al.[37] equilibrium shift towards the aldehyde is favoured by increase in temperature.
Scheme 1. Possible conversion routes of hydroxyacetone.
(>30°C) and acidity of the solution. Hydrogenation of HYDA results in formation of 1,2-PDO (route 4) [20, 38]. Hakim et al. [30] studied HYDA conversion over CeZrO₂ catalyst and formation of 1,2-PDO was observed without external hydrogen input. These authors proposed that transfer hydrogenation reaction takes place between to HYDA molecules producing pyruvaldehyde and 1,2-PDO. Wawrzetz et al. [20] reported 1,2-PDO to be one of the major products in liquid phase during APR of HYDA over Pt/Al₂O₃ catalyst. It is also possible to form 1,2-PDO via the enol form of HYDA followed by hydrogenation (via route 3 and 3b). Further 1-propanol can be produced from 1,2-PDO via hydrogenation (route 4b). Dehydration followed by hydrogenation of HYDA results in acetone (route 5). In addition, acetone can also be formed via acetic acid ketonization that would release CO₂ as by-product (not shown) [39]. Acetone can further condensate to coke precursors over the supports by aldol condensation reaction [23-25]. HYDA can also undergo aldol condensation by itself (route 6). Our recent ATR-IR work demonstrated that aldol condensation is the most pronounced pathway over ZrO₂ under APR conditions [40]. Intermolecular reactions e.g. between acids (e.g., lactic, acetic acids) can give rise to C₄ oxygenates.

The main components observed in the aqueous phase indeed, following these discussions are, acetic, acid, 1,2-PDO, LA, ethanol and 1-propanol. Scheme 1 shows further possible routes via tertiary reactions, however, as we do not see them in our HPLC analysis of the aqueous phase, they must be either not present in detectable amounts or higher MW components marked in scheme as condensation products. In the sections below, performance of the catalysts is correlated to the reaction pathways that HYDA can follow during APR as discussed above.

4.2 Carbon to Gas Conversion, hydrogen yields

In the absence of catalysts, and even in the presence of only supports, Carbon to Gas Conversions were low (Table 3), most of the conversion was towards products in the liquid phase indicating that APR of HYDA requires Pt for efficient conversion to syngas, hydrogen.

Intrinsic activity for hydrogen formation (TOF) was high for Pt supported on Al₂O₃OH or C. Pt/C performed the best for gasification (Table 4), but also for H₂ production despite of the higher CO yield compared to Pt/Al₂O₃(OH). Similar trends in activity between Pt supported on Carbon or oxides have been reported in the past [6, 41]. Typically, lower rates for APR are often assigned to i) structure sensitivity (metal particle size sensitive) [6, 42, 43], ii) mass transfer issues either in liquid phase of various oxygenates or in gas phase by hydrogen formed being consumed in side reactions due to diffusion effects [44], iii) metal-support interplay (e.g. hydro-deoxygenation). The Pt size of the catalysts decreased in order Pt/Al₂O₃OH > Pt/C > Pt/ZrO₂ (chemisorption). Pt size difference between Al₂O₃OH and Carbon supported catalysts was only minor compared to ZrO₂ supported. Pt particle size has been reported to have an influence on the increased hydrogen selectivity by Lehnert and Claus [43] who studied APR of glycerol over different alumina supports. However, nothing was mentioned about
catalyst deactivation profiles. They suggested that C-C cleavage in oxygenates are preferred on face atoms rather than on edges and corners. As Pt particles size increases the number of face atoms increases and in turn favors C-C cleavage that competes and reduces H₂ selectivity. Kirilin et al. [6] reported increased TOF for hydrogen with increasing metal size on Pt/C in APR of xylitol. Their results were in good agreement with Lehnert and Claus. Also Ciftci et al. [42] reported Pt size dependency for Pt/C catalysts in glycerol APR. In a Pt size domain of 1.2 to 4 nm, the optimal TOF for H₂ and C-C cleavage rate was obtained with approximate Pt size of 2nm (measured with TEM). However, contradictory suggestion have been made in literature [20, 45]. It has been reported that with increasing Pt size the dehydration/hydrogenation reactions increase and in turn promote formation of alkanes with the expense of hydrogen[20]. In our case, small Pt size on ZrO₂ could contribute for the lower gasification activity. Mass transfer limitations could also affect the product yields and observed performance [44]. To rule out effect of internal mass transfer we tested Pt/ZrO₂ in the same conditions with lower grain size fraction and observed similar performance (data comparison is shown in Supplementary information Figure S1). Effect of mass transfer therefore for the low APR activity of Pt/ZrO₂ can be ruled out.

Most undesired products in APR are formed by interplay of the support and metal on the reacting molecule. For instance, in hydro-deoxygenation (HDO), support is responsible for dehydration and metal for the hydrogenation. Important property of the support to carry out this kind of reaction is acidity/basicity. This is discussed later.

The activity of supports in APR were measured and the results were shown in Figure 6 and 9, earlier. Carbon support had similar activity as Thermal, therefore we assume that it had minor effect on the products over Pt/C, hence Pt did most of the work. Over Al₂O₃ liquid phase products were enhanced compared to thermal, products requiring C-C bond breakage and reduction, such as ethanol, were observed. However, over Pt/Al₂O₃, ethanol amount was reduced. We suggest that this is due ability of Pt to reform further the intermediates formed over the support. Over ZrO₂ support activity in dehydration and coupling is substantial and it overcame the activity of the metal. Pt influence is seen in the increased CO₂ formation, but more clearly in formation of CH₄, however the Carbon to Gas Conversion rates are only a fraction of the ones observed for the other catalysts. Considering this analysis the more inert the support is, the better rates for Carbon to Gas Conversion can be observed.

Furthermore, the higher activity of ZrO₂ support itself towards non-gaseous phase, aqueous phase, and coke/char lowers hydrogen yields. Zirconia is reported to facilitate internal hydrogen transfer reactions [30]. Such conversion in the case HYDA results in PDO formation as discussed earlier. Comparing Figures 5 and 6, it becomes clear that ZrO₂ results in high amounts of 1,2-PDO, as expected. Even in the presence of Pt (Pt/ZrO₂ catalyst) the amount of PDO formed are similar. This might be indication that PDO is more difficult to convert under the current APR conditions and thus lowers hydrogen yields. Interestingly, such internal hydrogen transfer reactions are not reported over Al₂O₃(OH) or C supports. Figure 6 supports this fact showing very little 1,2-
PDO. In the presence of Pt, amount of 1,2-PDO is increased as expected from hydrogenation by Pt (route 4 in Scheme 1), and due to its lower activity, 1,2-PDO remain in the liquid phase. It is important in the design of catalysts to be able to reform all oxygenates found in the aqueous phase to maximize hydrogen yields. In addition to lowering the hydrogen yields they can also undergo secondary conversions to products that deactivate catalysts [46].

Additionally, formation of alkanes lower hydrogen yields, further. As mentioned earlier, APR conditions are thermodynamically favourable for methanation and FT reactions. The former results in methane and latter higher hydrocarbons. As seen in Figure 4, methane is the dominant by-product for hydrogen consumption. In literature, it is commonly expected that Pt is not very active for FT [47], but it is a methanation catalyst and the activity towards methanation depends on the metal-support interaction [48-50]. For metals such as Pt or Pd the stronger the interaction between the support and the metal, the higher methanation activity. However in most cases a high methanation activity for Pt is found with Pt/TiO₂ catalyst due a special interaction with the support and metal [49]. In general, in APR the more basic the support or reaction medium, the more hydrogen selectivity is enhanced [51-53]. This behavior is explained for the support basicity as they contain more low coordinated O⁻ anions and with contact with H₂O they form OH-groups [54] which are expected to be in key role in WGS reaction [55]. Basic reaction medium in turn can polarize water more and enhance the WGS by creating OH-groups prone to adsorb on the catalyst surface [54, 56]. In our case (see Table 2), PZC of Carbon, was 2 and for Boehmite it was 8 (Table 2). This suggests very different surface properties for the supports despite that the methane amounts of the two catalysts were similar. This implies that the surface structure of the catalytic material did not play a key role in the methane formation.

![Graph showing hydrogen and methane yields compared over the catalyst tested in APR of 2.4wt% HYDA at 225°C/35bar.](image)

Figure 11. Hydrogen and methane yields compared over the catalyst tested in APR of 2.4wt% HYDA at 225°C/35bar.
Furthermore, formation of methane and hydrogen does not have an inverse relationship, but just the opposite. Hydrogen to alkane ratio is almost the same for all catalysts as can be seen in Figure 11. This seem to indicate that methanation (hydrogenation) of CO₂ does not seem to be the route to methane or FT route to higher alkanes. Other routes to methane are (i) stoichiometric decomposition of carboxylic acids (\(\text{CH}_3\text{COOH} = \text{CO}_2 + \text{CH}_4\)), route X, in Scheme 1 (ii) hydrogenation of intermediates adsorbed on the catalyst (e.g. route 1x on Scheme 1) (iii) hydrogen redistribution forming methane/alkanes and olefinic/aromatic precursors to coke. If hydrogen is not lost by methanation/FT, it should be consumed in other reactions. From Scheme 1, the major conversion routes for HYDA via hydrogenation are formation of 1,2-PDO and propanol and ethanol. Indeed, these products are the major components in the liquid phase. Table 7 shows extend of formation of these components from HYDA taking into account the hydrogen consumed when formed from HYDA. Surprisingly, over Pt/ZrO₂ hydrogen consumption for forming these components is the highest. Accordingly, yield to hydrogen is lowest for Pt/ZrO₂. Thus, yield to hydrogen seems to be determined by hydrogenation of HYDA and intermediates formed therewith in the liquid phase than methanation or FT reactions. Ideally in APR only \(\text{H}_2\) and \(\text{CO}_2\) should be formed, the latter formed via WGS. For both Pt/C and Pt/AlO(OH) methane was formed despite the good APR activity. As methanation of \(\text{CO}_2\) is not an issue, methane is formed via other routes (Scheme 1). In fact, all the liquid phase products formed can contribute to methane yields via incomplete APR since intermediate such as \(\text{CH}_3\) adsorbed on the catalyst (e.g. Scheme 1, highlighted box A) can be hydrogenated. Moreover, CO conversion via WGS seems not to be the active route in the case of Pt/C. Typically in gas phase, it is assumed that WGS requires bifunctional pathway, as \(\text{H}_2\text{O}\) is activated on the support and CO on the metal \([25, 57]\). The CO yield over Pt/C carbon was significantly higher than over Pt/AlO(OH) suggesting that conversion of CO to \(\text{CO}_2\) over Carbon supported catalyst is not as efficient. Despite this, the rates to \(\text{H}_2\) were still similar pointing out the advantage of the carbon supported catalyst. With improved WGS, \(\text{H}_2\) production on Pt/C could be even higher and very promising. de Vlieger et al.\([58]\) alloyed Ni with Pt/\(\gamma\)-Al₂O₃ and reported remarkably enhanced hydrogen selectivity.

<table>
<thead>
<tr>
<th>Component</th>
<th>Takes up (\text{H}_2)</th>
<th>Used (\text{H}_2)/HYDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOAc</td>
<td>1</td>
<td>Pt/AlO(OH) 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/C 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/ZrO₂ 0.07</td>
</tr>
<tr>
<td>EtOH</td>
<td>2</td>
<td>Pt/AlO(OH) 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/C 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/ZrO₂ 0.15</td>
</tr>
<tr>
<td>1,2-PDO</td>
<td>1</td>
<td>Pt/AlO(OH) 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/C 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/ZrO₂ 0.08</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>2</td>
<td>Pt/AlO(OH) 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/C 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/ZrO₂ 0.11</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.42</td>
</tr>
</tbody>
</table>

Table 7. Consumed \(\text{H}_2\) for liquid phase products per converted HYDA moles.
Stable catalyst supports for APR of hydroxyacetone

compared to monometallic Pt/γ-Al₂O₃ catalyst. It was suggested that the improved performance was due to enhanced WGS. Under oxidizing conditions like in APR, nickel forms NiO which is able to activate water thus, promote WGS and therefore increase H₂ selectivity. Enhancing the WGS activity of Pt/C is a relevant challenge to be followed. Furthermore, replacing some of the Pt with non-noble metal like Ni would also bring down costs for the catalyst.

In addition to being able to make hydrogen efficiently, the formation of products in the liquid phase can also affect the stability of the catalysts by secondary oligomerization reactions. Stability of the catalysts is discussed in this case in the following section.

4.3 Stability of the catalysts during APR

Stability of the catalysts during APR is as discussed in the introduction, reported to be challenged due to a variety of factors such as loss of catalytic material (leaching of support/metal) or by sintering of support due to phase transformations. Furthermore, catalytically active sites can be lost during reaction via coking or by sintering of the metal.

Figure 7 shows that Pt/Al₂O₃(OH) and Pt/ZrO₂ deactivated rapidly and Pt/C showed stable activity. Comparing the values from the Tables 2 and 5 leaching of Pt or support is not an issue for the three catalysts. Changes in the structure of the support can also be ruled out looking at XRD patterns of the fresh and spent catalysts presented in Figure 12. Thus, deactivation should result from loss of active sites via sintering or blockage by carbonaceous specie. For Pt/Al₂O₃(OH) C-analysis of the catalyst and the

![Figure 12. XRD patterns of the fresh and spent catalysts.](image)
support showed presence of carbon on the surface. Interestingly, conversion of HYDA over ALO(OH) remained stable, yet Pt/ALO(OH) suffered from severe deactivation. Takagagi et al. [59] reported stable performance of Boehmite in lactic acid production after humins were formed on the support. They suggested that humins blocked the surface sites for further condensation, which resulted in stable performance. This agrees with our observations C-C coupling reactions occur during HYDA conversion over ALO(OH) as seen in formation of butyric acid; over Pt/ALO(OH) this was less pronounced. Ketonization of butyric acid with other organic acids can create ketones with longer carbon chains (up to C7). Furthermore, alkanes were formed (C1–C3) also with small amount of unsaturated species (Figure 4). Based on TPO, carbon deposits on ALO(OH) materials had oxidation temperature closer to what is observed with dry reforming of methane [46-48]. The liquid products formed, such as acetic acid, acetone, ethanol, 1-propanol are reported to result in formation of carbonaceous species on oxide catalysts [23, 60]. Furthermore, formation of alkanes (C2 and C3) indicate that the catalyst was active in dehydration of oxygenates (e.g. alcohols) which would produce olefins as intermediates [61-63]. Bifunctional catalysts are often prone to coking under reactions with olefins [64]. We suggest that polymerization of these low oxygen containing intermediates over the metal caused the coke deposits. Furthermore, both spent oxide supported catalysts were tested after regeneration in the APR of HYDA and similar performance than with fresh catalyst was observed. Coke formed over Pt/ALO(OH) had higher oxidation temperature than the one used for the regeneration. Despite this most of the carbon was removed (Table 6) and the coke remaining did not affect the performance of the regenerated catalyst which indicated that it was not formed on the vicinity of the active sites. Furthermore, characterization (chemisorption, TEM) did not show loss of Pt surface area during catalysis (Tables 2 and 5) and therefore the deactivation by sintering can be ruled out.

In the case of ZrO2 catalysts both coking and sintering was observed, also the bare support suffered from deactivation. In ATR-IR experiments [40] aldol condensation products were observed to remain over the ZrO2 surface after the HYDA feed was changed to water confirming that carbon deposits are caused by condensation reactions. Supporting this, TPO results showed carbon deposits as condensation products (Figure 9.). Interestingly, looking at Figure 7 Carbon to Gas Conversion was stable after initial deactivation. Ketonization of carboxylic acids are known to release CO2 which ZrO2 is reported to perform [25, 39]. In addition, the bare ZrO2 was producing gas phase (mainly CO2) confirming this, see Table S2 Supplementary information. It is also reported in the literature that ketonization activity was not significantly affected by the aldol condensation over CeZrOx when feeding acetic acid and HYDA [30]. We suggest that the observed stable Carbon to Gas Conversion is result of the gas released due to ketonization and not by APR.

Decrease in metal dispersion indicated that second cause of deactivation was loss of active surface area by sintering over Pt/ZrO2. As mentioned, APR with the regenerated catalysts showed similar activity than the fresh ones. This indicates that the deactivation of both oxide supported catalysts was caused by coking and blockage of active sites. For
Pt/ZrO₂ the sintering of metal possibly occurred during the startup of the experiment and therefore did not affect our observations during measurement.

TOS activity of Pt/C showed stable performance. The carbon balance indicated absence of carbon deposits and post-catalysts characterization of the catalyst also supported the fact that the properties of the catalysts where not affected during APR. Pt/C shows good activity in the gasification of HYDA, but had a low WGS activity. Improving WGS with alloying Pt with e.g. Ni [58] makes Pt/C a good candidate as APR catalyst of complex feedstocks.

As suggested earlier, acidity is a key factor in condensation reactions and coking. For instance, acetic acid condensation to acetone (Eq. 7) and further to di-acetone alcohol (Eq. 8 and 9) results in unsaturated species (Eq. 10; MO, Mesityl oxide) that can further oligomerize to carbon deposits on the catalyst surface. This leads to deactivation and blocking of active sites [24]. It can be expected that hydroxyacetone undergoes these same condensation reactions over highly reactive oxide supports, such as ZrO₂ and AIO(OH). These are illustrated also in Scheme 1 equation 6.

\[
2\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (7)
\]
\[
2\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_2\text{COHCH}_3 (\text{enol}) + \text{CH}_3\text{COCH}_3 \quad (8)
\]
\[
\text{CH}_2\text{COHCH}_3 (\text{enol}) + \text{CH}_3\text{COCH}_3 \rightarrow (\text{CH}_3)_2\text{C(OH)CH}_2\text{COCH}_3 (\text{diacetone alcohol}) \quad (9)
\]
\[
(\text{CH}_3)_2\text{C(OH)CH}_2\text{COCH}_3 (\text{diacetone alcohol}) \rightarrow (\text{CH}_3)_2\text{C} = \text{C(CH}_3\text{COCH}_3 (\text{MO})
\]
\[\text{+ H}_2\text{O}\]

(10)

To help confirm our hypothesis for the coking and deactivation, we investigated the acidity of the oxide catalysts. The oxide supported catalysts were characterized by pyridine FTIR and by temperature programmed desorption with NH₃. FTIR spectra of pyridine adsorbed on Pt/ZrO₂ and Pt/AIO(OH) after evacuation at room temperature (RT) and 225 °C and then followed by cooling down to 25 °C are shown in Figure 13. For Pt/ZrO₂ peaks of higher intensity were seen compared to Pt/AIO(OH). Intensities of all of the peaks decreased after evacuation at 225 °C, in particular for Pt/AIO(OH). Comparing to literature[65, 66] our peak assignments it was concluded that Pt/ZrO₂ has Lewis acidity (LPy; 1605 and 1456 cm⁻¹) and weak Brönsted acidity (BPy; 1641cm⁻¹), as well as Lewis basicity (LB, Py-oxx₁ and Py-oxx₂ 1488, 1548 cm⁻¹). Py-oxx₁ and Py-oxx₂ were assigned to pyridine oxidation species (carboxylate and carbonaceous species, respectively) based on the observation of Zaki et al. [65] that these species can be formed on metal oxides due to presence of Lewis basic sites at temperatures above 100°C. For
Figure 13. FTIR spectra after pyridine adsorption on Pt/ZrO$_2$ (a, b) and Pt/AlO(OH) (c, d) after evacuation at RT (b, d) and 225°C (a, c).

Pt/ZrO$_2$ pyridine was also found in hydrogen-bonded state (HPy) according to peaks at 1593 and 1442 cm$^{-1}$.

After evacuation at 225 °C, LPy shifted to 1608 cm$^{-1}$, but BPY almost disappeared suggesting the presence of weak and strong Lewis acid sites and weak Brönsted acid sites. Intensities and rates of disappearance of BPY compared to LPy suggest that Pt/ZrO$_2$ has more Lewis acid sites than Brönsted acid sites.

Pt/AlO(OH) has Lewis acid sites (LPy; 1616, 1492 cm$^{-1}$) [65] and no Brönsted acidity, as well as no Lewis basicity which is in agreement with the results reported earlier [67] However, hydrogen-bonded pyridine was detected as well (HPy; 1595, 1577 and 1446 cm$^{-1}$). The peak shift of LPy to 1622 cm$^{-1}$ after evacuation at 225°C suggested that both weak and strong Lewis acid sites are present on Pt/AlO(OH). Compared to Pt/ZrO$_2$, Pt/AlO(OH) had less intense peaks in all spectra as well as lower surface area, which suggested a lower surface concentration of Lewis sites on Pt/AlO(OH). Interestingly, acidity of Pt/AlO(OH) was similar to Pt/Al$_2$O$_3$ (See Supplementary information in S2) despite the differences in Al coordination.

TPD NH$_3$ profile of Pt/ZrO$_2$ revealed two peaks centered at 93°C and 329 °C (Figure 14), corresponding to the total acidity of 604 mmol/g. TPD NH$_3$ profile of Pt/AlO(OH) showed a small peak at 97 °C and a very intense peak at about 500 °C with a shoulder at 300 °C. The total acidity of Pt/AlO(OH) during NH$_3$ desorption could not be accurately calculated due to interference from H$_2$O in TCD signal at 500 °C, which is
most likely due to water desorbing as a result of phase transformation of AlO(OH) into \( \gamma\)-Al\(_2\)O\(_3\) happening at this temperature [68-70].

Carbon supported catalysts are typically reported to have much lower acidity than oxides[6]. The supports have functional groups such as carboxylic acid, hydroxyl, ketone, anhydride or lactone groups [71] which makes the supports hydrophilic. We measured the point of zero charge (PZC) of the support material and found it to be 2, this indicates that the surface has functional groups. However, the activity of these groups in catalysis under APR conditions is questionable. In literature, carbon used also in our experiments is reported to have no acidity without metal[72]. Considering the stability of the catalyst, the good carbon balance during the experiment and low levels of liquid products formed, it is unlikely that the Pt/C suffered from carbon deposits or coking. For designing an efficient and stable catalyst for APR of complex biomass feeds it is essential to use materials that do not promote condensation and coking reactions. The carbon supported catalyst showed promise for it.

5 Conclusions

An attractive APR catalyst gives maximized H\(_2\) yield at relevant conversion levels and possesses stable performance. This work illustrates that by minimizing formation of liquid phase products this can be approached. Acidity of the support, both Bronsted and Lewis, has a strong influence and need to be optimal. Zirconia supported materials enhanced formation of alcohols in the aqueous phase, which consumed the formed hydrogen plus facilitated condensation reactions to coke precursors leading to catalyst deactivation. With a challenging feedstock as HYDA a support material that suppresses these reactions is required. In our case carbon supported Pt catalyst performed the best. It was stable in APR of HYDA and had the best gasification activity with minimal
secondary reactions in the liquid phase. Initial hydrogen yield was lower than with Pt/Al2O(OH) due to low conversion CO to CO2 via WGS. Nevertheless, having stable performance offers a starting point to enhance the performance further to higher H2 yields.

6 References

[42] A. Ciftci, D.A.J.M. Lifheart, E.J.M. Hensen, Influence of Pt particle size and Re addition by catalytic reduction on aqueous phase reforming of glycerol for carbon-
supported Pt(Re) catalysts, Applied Catalysis B: Environmental, 174-175 (2015) 126-135.


101


Mass transfer effect in performance of Pt/ZrO₂ – comparison of two grain sizes.

The performance of Pt/ZrO₂ catalyst was significantly different from the other two catalysts and therefore the effect of internal mass transfer was ruled out by testing the same catalyst with smaller grain size for the APR of HYDA. As can be seen in the Figure S1 the conversion levels remained the similar during the course of the experiment and therefore we assume that the activity was not affected by internal mass transfer.

![Graph showing conversion levels for different grain sizes of Pt/ZrO₂ catalysts.](image)

Figure S1. Comparison of performance between Pt/ZrO₂ with two grain sizes. Filled upright triangle: Pt/ZrO₂ (300-600μm) Empty downright triangle: Pt/ZrO₂ (100-250μm).
Gas phase composition over ZrO$_2$ support

Table S1 shows gas phase composition over ZrO$_2$ support. As can be seen the main component in gas phase was CO$_2$ with very small amount of H$_2$ and CO.

Table S1. Gas phase yield over ZrO$_2$ support.

<table>
<thead>
<tr>
<th>Gas phase</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.7</td>
</tr>
<tr>
<td>CO</td>
<td>0.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.9</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0</td>
</tr>
<tr>
<td>C$_2$</td>
<td>0</td>
</tr>
<tr>
<td>C$_3$</td>
<td>0</td>
</tr>
</tbody>
</table>
Acidity of Pt/AlO(OH) and Pt/Al2O3 compared

Figure S 2.FTIR spectra of pyridine adsorption on Pt/AlO(OH) after evacuation at RT (a), 225°C (b) and on Pt/Al2O3 after evacuation at 50°C (c) and 150 C (d).
Chapter 6

Tuning the characteristics of Pt/C catalysts for APR of biomass related oxygenates

Carbon supported Pt catalysts are stable and viable catalysts for conversion of oxygenates in APR conditions. Catalyst properties determine the activity and selectivity among the conditions used. In this chapter, we study the effect of Pt particle size and distribution on the support on performance of the catalyst. The results showed that egg-shell type distribution and larger Pt size seems to enhance the activity of the catalyst and also increase the hydrogen turnover rate.

A.K.K. Vikla, I. Simakova, Y. Demidova, R. Keim, L. Lefferts, L. Calvo, M. Gillaranz Redondo, K. Seshan, Tuning the characteristics of Pt/C catalysts for APR of biomass related oxygenates (to be published)
1 Introduction

Aqueous phase reforming is a challenging process for a catalyst due to the drastic conditions used and complex feedstocks utilized. As discussed earlier in this thesis, the most suitable catalyst should be stable via resistance to coking and sintering of metal, Pt in the current study, particles under the hydrothermal conditions (225-275 °C/35-90 bar) used in APR. In Chapter 5, we demonstrated that Pt/C shows promise and is viable for APR conversion of Hydroxyacetone (HYDA) (Figure 1), a difficult oxygenate to gasify. HYDA is a challenging model component due to its tendency to form coke on the catalyst and cause deactivation, especially on oxide-supported catalysts. Pt/C, promisingly, showed to be an active catalyst for APR gasification compared to oxide supported Pt catalysts (Table 1). Enhanced gasification activity of Pt/C catalyst reduces the formation of liquid by-products, some of which are intermediates to coking.

The next steps for developing the Pt/C catalyst further for APR application would be to enhance hydrogen, syngas yields, optimise use of Pt to minimise costs for the catalyst.

Pt cost savings can be achieved by enhancing dispersion of metal and thus lowering metal particle size. Typically in catalysis, high dispersion of metal is preferred as it ensures smaller metal particles on the support creating more sites for catalytic activity. One way to achieve Pt size typically requires varying the loading of the metal [1]. However, there are other controllable means of changing the distribution of the metal on the support, such as modifying the application method of the metal or altering the calcination/reduction procedures of the catalyst [2-4].

![Graph showing the activity of Pt/C catalyst compared with Pt/AlO(OH) and Pt/ZrO2 for APR of hydroxyacetone (HYDA) under 225 °C/35 bar.](image)

Figure 1. Activity of Pt/C catalyst compared with Pt/AlO(OH) and Pt/ZrO2 for APR of hydroxyacetone (HYDA) under 225 °C/35 bar.
Table 1. Comparison of intrinsic activity (30 min) of Pt/C catalyst to Pt/AlO(OH) and Pt/ZrO₂ for APR of HYDA under 225 °C/35 bar. \(X_{i,30}\) is Total Conversion of HYDA at 30 minutes on stream, \(X_{G3C,30}\) is Carbon to Gas conversion \(X_{LQ,30}\) is Liquid Phase Conversion and CB\(\text{\textsubscript{30}}\) is carbon balance, all at 30 minutes time on stream.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(X_{i,30})</th>
<th>(X_{G3C,30})</th>
<th>(X_{LQ,30})</th>
<th>Coke</th>
<th>CB(\text{\textsubscript{30}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>52</td>
<td>39</td>
<td>12</td>
<td>n.a.</td>
<td>96</td>
</tr>
<tr>
<td>Pt/AlO(OH)</td>
<td>58</td>
<td>44</td>
<td>18</td>
<td>1</td>
<td>98</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>57</td>
<td>18</td>
<td>36</td>
<td>4</td>
<td>88</td>
</tr>
</tbody>
</table>

The interaction between the support and the metal is important, strong interaction prevents sintering/agglomeration of the metal particles. Changing the surface polarization of the support can alter interaction between Pt and carbon supports. This is often achieved by acid treatment of the support by introducing different oxygen containing polar groups on the surface of the catalyst [5, 6]. Pt is an expensive metal [7] and for industrial application one would prefer to use as small loading as possible to avoid high costs for the catalysts. However, using carbon as a support ensures that the metal is easier to harvest for recycling after usage as the carbon can be burned and metal collected [8].

Further, changing the Pt particle size as well as its interaction with the support can influence its catalytic properties. This can influence, in turn, the catalytic chemistry which can affect the product selectivities. In literature the effect of Pt size in relation to APR performance is discussed, however, the conclusions are contradictory. Lehnert and Claus [9] studied APR of glycerol over Pt supported on alumina. They suggested that C-C cleavage in oxygenates are preferred on face Pt atoms rather than on edges and corners. As Pt particle size increases, the number of face atoms increases, and in turn favours C-C cleavage over the competing C-O cleavage and increases H₂ selectivity.

Kirilline et al. [10] reported increased TOF for hydrogen with increasing metal size on Pt/C in APR of xylitol. Their results are in good agreement with Lehnert and Claus. Also Ciftci et al. [11] reported Pt size dependency for Pt/C catalysts in glycerol APR. In a Pt size domain of 1.2 to 4 nm, the optimal TOF for H₂ and C-C cleavage rate was obtained with approximate Pt size of 2 nm. Some reports have the opposite conclusions to these [1, 2, 12]. Wawrzelz et al. [1] studied glycerol APR by varying Pt size with Pt loading; Pt loading of 0.98 wt% resulted in average Pt size of 1.1 nm and the highest loading of 4.88 wt% Pt resulted in Pt size of 2.60 nm. The researchers reported that while glycerol TOF increased only slightly with Pt size, however, enhanced hydro-deoxygenation (HDO) reactions consumed hydrogen. Their conclusion was that while surface metal site concentration decreases, the dehydration/hydrogenation reactions increase and in turn promote formation of alkanes at the expense of hydrogen. Chen et al. [12]
investigated Pt size-effect in APR of low boiling point fraction of bio-oil. They used colloidal-Pt particles as precursor for loading the metal on the support and were therefore able to vary Pt size without altering the Pt loading. Pt size was varied between 1.6 nm and 5.7 nm. They suggested that the edge sites of Pt particles were the main active sites for hydrogen production since the more defect sites (edge sites) are on the catalysts, the more Pt-C bonds (via C-C bond cleavage) can be formed. In contrast to previously reported, the surface sites are more effective for C-C-bond cleavage, here Chen et al. claim that edge sites are more favourable for the same. Increasing particle size and the corresponding increasing TOF by Chen et al. seem to contradict their conclusion that edge sites are favourable because larger particles would have more face sites. Based on their results the optimal Pt size was 2.6 nm. Pt-C bonding will enable C-C-bonds cleavage, which is the ideal route for H₂ formation as C-O cleavage will promote formation of alkanes (Chapter 2, Figure 8). Barbelli et al. [2] reported similar conclusion as Wawrztz et al. and Chen et al. In the studies reported above, the authors have compared results of catalysts with different metal loadings and sometimes different supports. Also, to our knowledge, no efforts have been made to understand the influence of Pt distribution on the support (homogeneous vs. egg-shell). In order to eliminate the probable effects of these parameters, it would be ideal to prepare catalysts with same support, and Pt loading and then vary particle size and metal distribution throughout the support.

In this chapter we investigate the effect of Pt distribution over a Sibunit carbon support and the effect of Pt particle size for the APR of Ethylene Glycol (EG). The catalysts were prepared in various ways in order to alter the Pt size on the support while keeping the Pt loading similar. Preparation methods have also been adapted to obtain different Pt distribution over the support. In order to compare straight forward the effect of Pt size for the catalyst performance, that is, conversion and especially product distribution, EG was used as a model component. EG is a simple oxygenate with both carbon atoms connected to OH-groups. This allows to estimate the catalysts preference for C-C and C-O cleavage.

The purpose of this study, is to understand the effects of the above variables on the APR of ethylene glycol and thus help optimise/provide basis for an efficient catalyst.

## 2 Experimental

### 2.1 Catalyst preparation and characterization

Catalysts were prepared with variable methods aiming at nominal loading of 1 wt% of Platinum on Sibunit mesoporous carbon (100-200 μm). The preparation methods are summarized in Table 2. Pt-IM and Pt-OX were prepared via incipient wetness impregnation with H₂PtCl₆ followed by drying in air overnight at 100 °C. After this, Pt-IM was reduced in H₂ at 320 °C for 6 hours. Pt-OX was obtained by calcining the dried sample at 420 °C for 6 hours followed by reduction in H₂ at 700 °C for 5 hours.
Table 2. Preparation methods of each catalyst summarized.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-IM</td>
<td>impregnation, drying, reduction at 320 °C</td>
</tr>
<tr>
<td>Pt-OX</td>
<td>impregnation, drying, calcination at 420 °C, reduction at 700 °C</td>
</tr>
<tr>
<td>Pt-PR</td>
<td>precipitation with Na₂CO₃ reduction with HCOOH, drying, reduction at 700 °C</td>
</tr>
<tr>
<td>Pt-CL</td>
<td>pre-prepared colloid impregnated, drying, treated in HCW 225 °C/35 bar</td>
</tr>
</tbody>
</table>

Catalyst Pt-PR was prepared by precipitation of H₂PtCl₆ with Na₂CO₃ followed by reduction in formic acid. The catalyst was then treated in H₂ at 700 °C for 5 hours. Catalyst Pt-CL was prepared using Pt-PVP colloid via wet impregnation and drying in air. After this, the catalyst was treated in hot compressed water (HCW, 225 °C/35 bar) by flowing 2 ml/min water over the catalyst for 1 hour while heating up to 225 °C, where after temperature remained constant. This sequence mimics the startup period for an APR the experiment and was used to remove the colloid on the Pt. After this treatment, the catalyst was removed from the reactor and dried. All catalysts were characterized as follows.

The catalysts were characterized by XRF, N₂ physisorption using the BET adsorption isotherm method and CO pulse chemisorption. Further, catalysts were characterized by XPS and TEM cross-sectional analysis (TEM-CS) to determine distribution of Pt on the catalyst grains as in an egg shell structure or in a more homogeneous fashion. Details of XPS method were explained in Chapter 3. Pt distribution analysis was also performed by measuring the samples as prepared (100-250 μm) and by grinding them to small fine powder (<40 μm). The Pt content in these samples would then give estimation of the distribution of the metal over the catalyst grains.

2.1.1 TEM cross-sectional imaging

Cross section imaging of the catalyst grains was performed by using TEM. A Philips CM300ST-FEG TEM instrument, operating at 300 kV acceleration voltage, was utilized to analyze the cross sectional TEM specimens.

TEM specimen preparation was accomplished by a slightly modified version of the established technique of dimple grinding and argon ion etching, and can be described in the following summarized way. The catalyst grains were embedded by mixing these into a two-component epoxy resin G1 (Gatan) forming a slurry. This slurry was then applied between two dummy silicon plates (4 mm x 5 mm in size) held in a sandwich structure, immediately followed by hardening at 120 °C. Subsequently, the fixed sandwich structure was cut into cross-sectional slices with a thickness of 1.5 mm. From this rectangular slice a circular disc was retrieved by a Gatan model 601 ultrasonic
disc cutter. The resulting disc was reinforced by embedding it in a copper ring. The copper reinforced disc was then abraded plane-parallel to 100 μm thickness in a stepwise fashion, using diamond grinding paper, starting with grit 500 and finishing with grit 4000. During this stage of mechanical thinning, special attention was paid to find a suitable grain around the center of the disc by continued grinding until approximately its maximum diameter was reached. When this was established by grinding from one side, the cross-sectional slice was turned over so that grinding could proceed from the other side, ultimately reaching a disc thickness of 100 μm. In some cases, however, it was necessary to repeat this flip-over a couple of times before a suitable maximum diameter grain position within the 1.5 mm thickness of the optically semi-transparent hardened glue layer was established. Mechanical thinning was continued using the Gatan model 656 dimple grinder. One side was only mildly abraded/polished a couple of minutes using a felt wheel, applying 1 μm and 0.25 μm diamond paste, respectively, followed by a 0.05 μm alumina suspension. The other side was dimpled by a 15 mm diameter stainless steel wheel using 1 μm diamond paste down to a thickness of 10 μm in the center of the disc, followed by grinding/polishing with the felt wheel, using 1 μm and 0.25 μm diamond paste, respectively, until a thickness of approx. 2 μm in the center of the disc was realized. A 0.05 μm alumina suspension for 2 minutes was used in the final polishing stage. Finally, the cross-sectional TEM specimen was thinned to electron transparency by means of the Gatan model 691 precision ion polishing system (PIPS), with an etching angle of 4° for the upper gun irradiating the large dimpled side, and 2° for the lower gun irradiating the flat polished side, applying an accelerating voltage of 4.2 kV in the initial stage of etching and 700 eV in the final stage.

Based on the images recorded during TEM-CS an average Pt cluster size was calculated. For Pt-PR and Pt-CL approximately 200 particles were counted. For Pt-IM approximately 50 particles were used.

### 2.2 Catalyst testing

Testing of the catalysts was carried out at 225 °C and 35 bar with 2.5 wt% ethylene glycol (EG, Sigma-Aldrich >99%). The experiments were carried out by using feed flowrate of 2 ml/min and 1 gram of catalyst. The details of experimental procedure were given in Chapter 3. After each experiment the heating was turned off and the feed solution was changed to distilled water. The reactor was allowed to cool down to room temperature, flowing water over the catalyst for two hours. The catalyst was collected the next day from the reactor and dried in a vacuum oven at 50 °C for 8 hours.
3 Results

3.1 General catalyst properties – metal loading, BET surface area and metal particle size

Properties of the fresh and spent catalysts are presented in Tables 3 and 4, respectively. The loading of the catalysts showed no major differences between fresh and spent, except for Pt-OX catalyst that seemed to lose part of the metal during experiment. BET surface areas of the fresh catalysts are relatively close to each other between 296-372 m²/g. The spent catalysts showed similar BET area, thus no major changes in the catalyst pore structure was observed.

CO chemisorption and TEM results indicate similar trends in Pt particle sizes when comparing the different catalysts. The absolute values according TEM and chemisorption however differ significantly and chemisorption seems to over-estimate the metal particle size. The difference may be caused by the difference in averaging, number averaged based on TEM and surface area averaged based on chemisorption. This will not be discussed in more detail here.

Comparison of Tables 3 & 4 show the effect of reaction conditions on the Pt metal. Clearly, all spent catalysts possess larger Pt particles according to both chemisorption and TEM; apparently operation in APR induces growth of Pt particles. Size distributions based on TEM measurements for the both fresh and spent catalysts are also shown below in Figures 2-6 with TEM micrograph images. For all the catalysts larger particles appear after APR experiment and flattening of the distribution occurs. The agglomeration can also be seen from the TEM images. The biggest change in distribution occurred with Pt-PR catalyst (Fig. 4), the distribution changed from average mean Pt size of 3.2 nm to 8.3 nm with large Pt particles also present (20-40 nm). The smallest change was with Pt-OX catalyst, the distribution flattened slightly and agglomeration was visible in TEM images (Fig 3) however, compared to the other catalysts, this change was the smallest.

Table 3. Properties of the fresh catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading wt%</th>
<th>BET m²/g</th>
<th>CO chem D %</th>
<th>Pt size, nm</th>
<th>TEM nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-IM</td>
<td>1.2</td>
<td>368</td>
<td>31</td>
<td>2.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Pt-OX</td>
<td>1.4</td>
<td>340</td>
<td>29</td>
<td>2.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Pt-PR</td>
<td>0.8</td>
<td>372</td>
<td>22</td>
<td>4.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt-CL</td>
<td>0.7</td>
<td>296</td>
<td>30</td>
<td>3.9</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 4. Properties of the spent catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading wt%</th>
<th>BET m²/g</th>
<th>CO chem D %</th>
<th>Pt size, nm</th>
<th>TEM nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-IM</td>
<td>1.2</td>
<td>343</td>
<td>13</td>
<td>8.8</td>
<td>2</td>
</tr>
<tr>
<td>Pt-OX</td>
<td>1.2</td>
<td>326</td>
<td>34</td>
<td>3.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Pt-PR</td>
<td>0.7</td>
<td>343</td>
<td>11</td>
<td>10.7</td>
<td>8.3</td>
</tr>
<tr>
<td>Pt-CL</td>
<td>0.8</td>
<td>292</td>
<td>21</td>
<td>5.4</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Figure 2. Pt size distribution measured from TEM imaging for the Pt-IM catalyst as fresh and after APR experiment. TEM image A corresponds to the fresh catalyst and image B to the spent catalyst.
Figure 3. Pt size distribution measured from TEM imaging for the Pt-OX catalyst as fresh and after APR experiment. TEM image A corresponds to the fresh catalyst and image B to the spent catalyst.

Figure 4. Pt size distribution measured from TEM imaging for the Pt-PR catalyst as fresh and after APR experiment. TEM image A corresponds to the fresh catalyst and image B to the spent catalyst.
Figure 5. Pt size distribution measured from TEM imaging for the fresh Pt-CL catalyst. TEM micrographs A1 and A2 show the fresh catalyst with two magnification 50nm and 100nm.

Figure 6. Pt size distribution measured from TEM imaging for the spent Pt-CL catalyst. TEM micrographs B1 and B2 show the spent catalyst with magnification of 20nm.
3.2 Detailed characteristics of the catalyst - Pt distribution over the catalyst grains

The catalysts were characterized by XPS and TEM cross-sectional analysis. This was to gain more insight on the distribution of the metal though the catalysts grains. That is to know if an egg-shell structure was present in the catalysts.

3.2.1 XPS analysis

XPS analysis was performed to measure the composition of Pt on the catalysts grains as prepared (100-250 μm) as well as after grinding the samples to fine powder (<40 μm). In this way it was possible to determine whether the outer shell of the catalyst contains more Pt compared to the inner core. The results are shown in Table 5. The Pt content for Pt-PR shows higher concentration of Pt on the sample as prepared than on the ground sample. The Pt content was approximately 53% higher on the outer surface than on the inner based on the measurement. Pt-CL - sample showed more dramatic difference. The Pt content was 5 times higher on the surface of the catalyst as prepared than on the ground catalyst sample. However, grinding did not significantly influence Pt-IM and Pt-OX.

3.2.2 TEM cross-section imaging

TEM cross-section imaging (TEM – CS) was performed for the catalysts to gain more visual evidence of the possible egg-shell structures. The egg-shell distribution would be visible if more Pt would be found on the edge structure than on the core of the grain.

Table 5. Elemental composition of the fresh catalysts measured by XPS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sample grain size</th>
<th>Elemental composition</th>
<th>Pt content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>wt%</td>
</tr>
<tr>
<td>Pt-IM</td>
<td>100-250 μm</td>
<td>0.08</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>powder &lt;40 μm</td>
<td>0.07</td>
<td>1.12</td>
</tr>
<tr>
<td>Pt-OX</td>
<td>100-250 μm</td>
<td>0.08</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>powder &lt;40 μm</td>
<td>0.08</td>
<td>1.28</td>
</tr>
<tr>
<td>Pt-PR</td>
<td>100-250 μm</td>
<td>0.17</td>
<td>2.67</td>
</tr>
<tr>
<td></td>
<td>powder &lt;40 μm</td>
<td>0.11</td>
<td>1.74</td>
</tr>
<tr>
<td>Pt-CL</td>
<td>100-250 μm</td>
<td>0.74</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>powder &lt;40 μm</td>
<td>0.13</td>
<td>2.04</td>
</tr>
</tbody>
</table>
In Figures 7-10 the TEM images recorded during cross-section analysis of catalyst grains.

Images from TEM- CS of Pt-IM are shown in Figure 7. Images A and B shows the grain edge and the grain core. Small Pt particles were observed and they were evenly distributed on both sites. The situation changed for the spent catalyst, on the catalyst grain edge (image C) large clusters were formed. The diameter is approximately 100 nm and 50 nm for these clusters. Scanning of the edge area further revealed few bigger Pt particles with sizes from 20 to 50 nm, but in total the big clusters were small in numbers.

Figure 7. Images from TEM cross-section analysis. A) TEM image of fresh Pt-IM catalyst at the grain edge, B) fresh Pt-IM catalyst imaged at the grain core, C) TEM image of the spent Pt-IM catalyst at the grain edge and D) spent Pt-IM catalyst imaged at the grain core.
Tuning the characteristics of Pt/C catalysts

Figure 8. Images from TEM cross-section analysis performed on Pt-OX catalyst. A) fresh Pt-OX catalyst viewed at the grain edge. B) fresh Pt-OX catalyst viewed at the grain core.

The smaller Pt particles found in these images corresponds to the average size measured in the conventional TEM imaging (See Tables 3 & 4). Measurements of the core area (image D) did not show any clusters or large Pt particles.

The Pt-OX imaging (Figure 8.) shows for the edge (A) and core (B) well dispersed small particles. Neither clusters nor large Pt particles were observed for the fresh catalyst. The spent catalyst was not measured since, no egg-shell structure was observed in XPS and the activity of the catalyst was poor.

Pt-PR is shown in Figure 9. Images A and B shows the fresh catalyst from the grain edge and grain core, respectively. As can be seen the grain edge had Pt particles distributed fairly evenly, but Pt particles with relatively high size were also observed. Pt particles measured were on average 11 nm but particles as large as 44 nm were also found. In addition, smaller particles that correspond more to the ones measured by the conventional TEM imaging were observed. The grain core (image B) shows even distribution of small particles similar Pt size as measured with the conventional TEM method (Table 3). Images C and D shows the imaging of the spent catalyst from the core edge and the core grain, respectively. The core edge shows the agglomeration of Pt after APR experiment, the averaged cluster size increased from 11 nm to 20 nm.

Figure 10 shows TEM–CS images of the Pt–CL catalyst. Fig A represents the grain edge of the fresh catalyst. As can be seen, from the edge of the grain to approximately 500 nm to inside of the grain, larger clusters of approximately 30 nm were formed. In addition, smaller Pt particles are observed down to of 3.6 nm (the averaged size). Image B shows the fresh catalyst from the core with fairly even distribution of Pt with the averaged size. Image C shows the spent catalyst from the grain edge with similar distribution of metal than with the fresh catalyst. The clusters showed some
agglomeration compared to fresh ones as Pt size increased from 24 nm to 30 nm. The grain core showed Pt particles at higher magnification (D1), but to a less density than fresh one.

Figure 9. Micrographs from TEM-CS imaging of the Pt-PR catalyst. A) Fresh catalyst viewed on the grain edge. B) Core of the fresh catalyst shown. C) Spent catalyst shown from the core edge. D) Core of the spent catalyst shown.
Figure 10. In images A and B the fresh Pt-CL catalyst is shown from grain edge and grain core, respectively. Images C and D shows the spent catalyst from grain edge and grain core, respectively.

3.2.2.1 Egg-shell type catalysts – summary of catalysts properties based on TEM-CS and XPS analysis

Catalyst Pt-PR and Pt-CL showed clear differences in Pt distribution between the catalyst edge and the catalyst core, for all of them images at lower magnification revealed that larger Pt particles were concentrated on the edges of the grains. This is illustrated for the spent Pt-PR and Pt-CL – catalysts in Figure 11.
In Table 6 averaged cluster size of the analyzed samples (TEM-CS) are shown with comparison to TEM Pt size. The table also shows the level of egg-shell distribution in all the catalysts based on XPS. Fresh Pt-IM had no clusters to be found in the TEM-CS however, the spent catalyst showed formation of Pt clusters, with average size of 17 nm. Pt distribution in XPS analysis showed no egg-shell structure. Pt-OX also showed no clusters for the spent catalyst in TEM-CS and by conventional TEM rather small increase in Pt agglomeration was observed. XPS showed no egg-shell distribution. Pt-PR showed increase of the cluster size from 11 nm to 21 nm between the fresh and spent, similar trend was also observed with the conventional TEM imaging. Presence of egg-shell structure was also indicated by XPS for this catalyst. Pt-CL had very clear clusters on the outer edge of the catalyst, which was very visible also in the XPS analysis. This catalyst had the highest degree of egg-shell type.

Table 6. Summary of averaged cluster size (TEM-CS) versus Pt size measured by TEM and Pt distribution as a level of egg-shell structure.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cluster size (TEM-CS)</th>
<th>Pt size (TEM)</th>
<th>Pt distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh (nm)</td>
<td>Spent (nm)</td>
<td>Fresh (nm)</td>
</tr>
<tr>
<td>Pt-IM</td>
<td>-</td>
<td>17</td>
<td>1.4</td>
</tr>
<tr>
<td>Pt-OX</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
</tr>
<tr>
<td>Pt-PR</td>
<td>11</td>
<td>21</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt-CL</td>
<td>24</td>
<td>30</td>
<td>3.6-</td>
</tr>
</tbody>
</table>

122
3.3 Catalyst performance in APR of Ethylene Glycol

Results of the catalyst testing are summarized in Table 4. Results are averaged from measured values from 210 to 420 minutes time on stream (TOS). In this time interval catalyst activity was steady and showed no deactivation. Pt-PR and Pt-CL showed the highest Total Conversion (X_t) on TOS. Initial as well as the steady state activity is decreasing in the order Pt-PR ≈ Pt-CL > Pt-IM > Pt-OX. In all cases Carbon to Gas (X_G2G) was slightly lower than total conversion, thus small amount of reactant was converted to liquid phase products (X_LQ). Overall, the conversion levels are relatively similar between the catalysts, expect Pt-OX, that had about 6-11% lower conversion level than the others. Mass balances were relatively good, 97-101%.

Catalyst performance as TOS is shown in Figure 12 in terms of Total Conversion (X_t). As can be seen no major deactivation occurred. Most catalysts underwent a slight drop in Total Conversion (2-3%) from the start of the reaction which seems to stabilize after 240 minutes of the reaction.

Figure 13 shows the yield to gas phase products at a steady state condition, averaged between 210 to 420 minutes. The products observed were H_2, CO, CO_2 and CH_4 from which the H_2 is the most interesting to us.

H_2 yield were in order Pt-PR > Pt-IM > Pt-CL > Pt-OX. The yield to CO was high in each case (18-25%) indicating lack of Water-Gas Shift reaction. The CO_2 levels correlate with this. CH_4 was the only alkane detected with low amounts less than 0.5% in each case.

In Figure 14 is the liquid phase products yields are presented. As with the gas phase products the data for these are also averaged during the steady state operation (data collection from 210 minutes to 420 minutes). The majority of products were alcohols and acids with minor amounts of aldehydes and larger polyol (glycerol). In all cases, yields to alcohols > acids >> aldehydes >>> polyols indicating influence of catalysts on the liquid phase chemistry during APR is similar.

Table 7. Averaged results of the catalyst testing (2.5 wt% EG, 225 °C/35 bar). The values are averaged from 300 to 420 minutes on TOS. X_t is Total Conversion of EG, X_G2G is Carbon to Gas conversion, X_LQ is Liquid Phase Conversion and CB is Carbon Balance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>X_t</th>
<th>X_G2G</th>
<th>X_LQ</th>
<th>CB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol%</td>
<td>mol%</td>
<td>mol%</td>
<td>mol%</td>
</tr>
<tr>
<td>Pt-IM</td>
<td>35</td>
<td>31</td>
<td>1</td>
<td>101</td>
</tr>
<tr>
<td>Pt-OX</td>
<td>25</td>
<td>23</td>
<td>3</td>
<td>97</td>
</tr>
<tr>
<td>Pt-PR</td>
<td>36</td>
<td>33</td>
<td>3</td>
<td>97</td>
</tr>
<tr>
<td>Pt-CL</td>
<td>36</td>
<td>34</td>
<td>6</td>
<td>97</td>
</tr>
</tbody>
</table>
Figure 12. Catalyst performance as time on stream (TOS) during APR of 2.5 wt% EG at 225 °C/35 bar.

Figure 13. Yield to gas phase products. Results are averaged from data collected between 240 to 420 minutes during APR of 2.5 wt% EG at 225 °C/35 bar.
Figure 14. Yields to liquid phase products during APR of 2.5 wt% of EG at 225 °C/35 bar. The data is averaged from time interval 240 minutes to 420 minutes of reaction.

4 Discussion

Catalyst used in this study were all prepared in different ways in order to alter the Pt size or its distribution on the support. The used methods did not only affect the Pt size, but also the loading and distribution of the metal on the support.

Especially application method of the metal on the support seemed to affect how evenly the metal was distributed over the support. Catalysts prepared by the more common method as incipient wetness impregnation (Pt-IM, Pt-OX), showed small metal particle sizes and more even distribution of metal. Catalyst prepared by precipitation (Pt-PR) and the more novel method by impregnation of pre-prepared colloid (Pt-CL) showed less homogeneous metal distribution. Metal distributions for these catalysts were closer to an egg-shell type of catalyst structure.

Temperature treatment, e.g. calcination, is often applied after metal is introduced to strengthen the metal-support interaction. In the case of carbon supported catalysts, drying in an inert gas is typically applied to avoid burning the support at high temperatures. Altering Pt size on Sibunit is challenging and therefore more drastic measures were also tried as the calcination for Pt-OX. This however, did not result in agglomeration of the metal.

All catalysts used in these study are based on Sibunit Carbon. This is a mesoporous carbon having a large surface area (∼350 m²/g). The material is stable during use for APR, as shown by lack of major changes in BET surface area. Separate experiments of treating Sibunit only in water under the APR experimental conditions for 8 hours also confirmed this observation. For these reasons, we assume that internal
diffusion limitation, if it plays any significant role considering the small reactant molecule used (EG) and even smaller products formed mainly, is similarly small for all catalysts. Any changes observed in chemistry of product formation should be related to Pt particle size or its distribution over the support. Influence of diffusion limitations for the catalysts were studied in detail and the results are presented in the next chapter. These studies confirmed absence of diffusional influence on the catalytic results for Pt/C catalyst.

The catalysts were all more or less stable during the APR of EG (Figure 7). No major deactivation was observed. However, when looking at the catalyst properties (Tables 2 and 3) it can be seen that for all catalysts only very small amounts of metal was lost. Thus, this is not significant.

Larger differences are seen when comparing the Pt sizes. All the catalysts are losing metal surface area during APR (Tables 3 & 4). A close look at TOS showed that catalysts initially deactivated slightly, but after 240 minutes TOS activity is stabilized (Figure 12). For comparing the effect of Pt size on the catalysts, we calculated activity based on available Pt surface area ($\mu$mol$_{E/G}$/m$^2$Pt$^2$min) and the results are shown in Figure 15. The values used for are based on averaged conversion levels from 240 minutes to 420 minutes of reaction and the dispersion based on post-mortem. The comparison showed that activity decreases in the order of Pt-PR > Pt-IM > Pt-CL > Pt-OX. Pt-PR showed the highest activity despite the larger Pt size (as seen from both CO chemisorption and TEM) and slight egg-shell character indicating that the larger Pt particles are more beneficial for EG conversion. Lehnert and Claus [9] suggested that C-C cleavage in oxygenates are preferred on face Pt atoms rather than on edges and corners. As discussed in the introduction when Pt particle size increases, the number of face atoms increases, and in turn favours C-C cleavage over the competing C-O cleavage.

![Figure 15. Activity of the catalysts ($\mu$mol$_{E/G}$/m$^2$Pt$^2$min) compared. The data is based on averaged activity from 240 min to 420 min and Pt dispersion at the end of the reaction.](image)
and increases H₂ selectivity. In general our results are in agreement with the suggestion of the increased TOF for larger particles. However, there will be an optimum and there will be a trade-off for activity as number of exposed Platinum atoms continues to decrease as the metal size increases.

In Table 7 we presented the average cluster sizes of Pt that was observed on the outer edges of the catalysts. To relate this to activity/H₂ selectivity we plotted the H₂ production rate (µmol/mₚt²*min) as a function of the cluster size of Pt (from post-mortem analysis), this is shown in Figure 16. This correlation suggests that the cluster size of 20 nm of Pt-PR is the most suitable for H₂ production under these conditions. Pt-CL has too high (31 nm) cluster size and Pt-IM too small. We assumed for this comparison that after the initial deactivation Pt agglomeration stopped and remain stable, therefore we are using the cluster size from the spent catalysts and average H₂ rate of formation (µmol/min) for the rate calculation. To know exactly when is Pt sintering occurring, one should monitor the catalyst in-situ. This is difficult to do during APR experiments due to the conditions used. The influence of the Pt agglomeration in H₂ rate for Pt-PR catalyst is shown in Figure 17. On the top of the left hand side Pt size with TEM micrograph and below it H₂ production rate at the beginning of the reaction (20 µmol/mₚt²*min). On the right hand side Pt size shown with the TEM micrograph and below it H₂ production rate at the steady state conditions (36 µmol/mₚt²*min). Increase in the Pt size does not sacrifice the hydrogen production, but enhances the rate per available Pt surface area.

Our results are consistent with what is reported in the literature. Results shown so far also indicate that, even though some mesoporous carbon was used in all cases and did not suffer any porosity changes, egg-shell type of distribution of Pt seem to be advantageous as these catalysts give the best conversion and hydrogen yields. These results are obtained with Ethylene Glycol, relatively small molecule, the advantage of
Figure 17. On the left hand side, initial hydrogen production rate (μmol/nm²pt*min) Pt particle size illustrated on the top (4.2 nm). On the right hand side H₂ production rate at steady state with the Pt size on top (10.7 nm).

egg-shell distribution should be significant for larger oxygenates which are typically present in the aqueous-phase of bio-oil.

Figure 18 shows turnover frequency for hydrogen (TOF-H₂). The TOF decreases in the order of Pt-PR > Pt-CL > Pt-IM > Pt-OX. What is significant is the high TOF of Pt-PR (275 molH₂/molpt*min). This is close to the one we presented in Chapter 4 with Pt/AlO(OH) (5 wt% EG, at 270 °C/90 bar), which indicated that Pt is working very actively on this surface. We see that (Figure 13) large amounts of CO are also formed during APR of EG. This indicates inefficient WGS conversion. Pt is not one of the best WGS catalysts and it is known that during WGS, CO is activated on metal and water on support, in all cases oxides, by forming hydroxyl groups. Adding a second metal such as Ni, which is an excellent WGS catalyst, we may be able to solve this issue. We have shown earlier [13] the Pt-Ni/Alumina was a very active, stable and selective catalyst for APR of EG. Creating polar oxygenates groups on the surface of C or even adding small oxide clusters may be ways to further improve the efficiency of Pt/C catalyst for enhanced hydrogen yields.

Table 8 gives a rough comparison of TOF-H₂ reported in the literature. All studies are based on APR of EG, but the experimental conditions, such as feed concentration, feed conversions, reaction temperature & pressure etc. vary drastically. However, in the absence of other data this gives a comparison of the state of the catalyst development.
Figure 18. Turnover frequency for hydrogen (TOF-H₂) averaged based on steady state conditions (240 min–420 min of reaction) and Pt dispersion.

From this table it can be seen that the top three catalysts for APR of EG are Pt/SiO₂ (Davda et al. [14]), vs Pt/ALO(OH) (us, Chapter 4) and Pt/C Sibunit C (us, this chapter). Stability of Pt/SiO₂ especially SiO₂ as it leaches under APR conditions, is a major issue in terms of long term catalyst stability. Pt/ALO(OH) is a good catalyst for APR of EG, as shown in Chapter 4. However with difficult feedstocks with tendencies for coke forming,

Table 8. Literature on H₂ TOF with difference catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Conc.</th>
<th>T/p</th>
<th>X</th>
<th>TOF-H₂</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>°C/bar</td>
<td>%</td>
<td>x10³ min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Pt/SiO₂</td>
<td>EG</td>
<td>5</td>
<td>210/20</td>
<td>9</td>
<td>75</td>
<td>A</td>
</tr>
<tr>
<td>Pt/SiO₂</td>
<td>EG</td>
<td>10</td>
<td>225/22</td>
<td>21</td>
<td>275</td>
<td>A</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>EG</td>
<td>1</td>
<td>225/29</td>
<td>90</td>
<td>0.08</td>
<td>B</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>EG</td>
<td>5</td>
<td>225/25</td>
<td>5</td>
<td>5.4</td>
<td>C</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>EG</td>
<td>10</td>
<td>225/29</td>
<td>5</td>
<td>6.7</td>
<td>C</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>EG</td>
<td>10</td>
<td>225/29</td>
<td>4</td>
<td>7</td>
<td>B</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>EG</td>
<td>5</td>
<td>270/90</td>
<td>43</td>
<td>60</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>Pt/AlO(OH)</td>
<td>EG</td>
<td>5</td>
<td>270/90</td>
<td>65</td>
<td>300</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>Pt/C (Pt-PR)</td>
<td>EG</td>
<td>2.5</td>
<td>225/35</td>
<td>36</td>
<td>248</td>
<td>This Chapter</td>
</tr>
</tbody>
</table>

B) Cotright et al. Nature 418 964–967
it shows deactivation by coking. We have shown this a due to the acidity of the support, ALO(OH). Pt/ALO(OH) deactivated rapidly for the APR of hydroxycetone (Chapter 5). Pt/C as we showed earlier was stable for also the APR of HYDA. Considering these issues, Pt/C is an excellent catalyst for APR of oxygenates. Having a high intrinsic activity for hydrogen and excellent stability, it is one of the most promising catalyst for further exploitation for APR of the aqueous phase of the pyrolysis oil or other waste aqueous oxygenate streams from other industries.

5 Conclusions

As shown earlier Pt/C is an efficient catalyst for APR of oxygenates. Sibunit support used for the catalysts in this study is a carbon material with stable pore structure (BET), therefore suitable as a support in the hydrothermal conditions of APR. Pt/C is the most promising catalyst based on this study due to its stability and hydrogen turnover comparing to catalysts reported in the literature such as Pt/SiO₂ and PtAl₂O₃. Using carbon as a support material allows also easier recovery of Pt compared to other expensive chemical methods. Pt distribution over the support revealed that egg-shell type of structure seemed to be more favorable. Furthermore, larger Pt particles appeared to be more active in C-C cleavage and improve hydrogen production. Further improvement of this catalyst is needed to enhance the WGS reaction. Pt/C is very promising catalyst for APR of the oxygenates typically present in waste water streams.

6 References

Chapter 7  
Investigation of diffusional effects in aqueous phase reforming of hydroxyacetone over Pt/C catalysts

Mass transfer limitations can affect the observed catalyst performance in different ways. In APR these limitations can alter the observed conversion rate or the product selectivities. We investigate these effects in this chapter for APR of 2.5 wt% hydroxyacetone. In addition, we calculated transport criteria to evaluate the existence of these limitations. Our results showed that external mass transfer effects were not present as the conversion rates of hydroxyacetone were not affected by the used conditions and the calculated criterion supported this. Internal mass transfer effects were not unambiguously excluded. However, Weisz-Prater criterion and the product selectivities showed small probability for their existence. Further, experiments at higher temperatures showed that WGS can be improved leading to higher hydrogen selectivity.

A.K.K. Vikla, Ö. Tuna, L. Lefferts, K. Seshan, Investigation diffusional effects in aqueous phase reforming of hydroxyacetone over Pt/C catalysts (to be published)
1 Introduction

Aqueous phase reforming is a promising process for converting low value oxygenates dissolved in water to syngas and hydrogen. The composition of industrial feedstocks, such as from food industry, pyrolysis process etc., are often complex and contain reactants with wide range of molecular weights. The diffusivity of these components in a porous catalyst can vary from each other. Limitations in the diffusion to the catalyst surface and to the active sites can have significant consequences. In a liquid phase, external mass transport limitation that can prevent the reactants efficiently reaching the catalyst surface would affect the observed conversion rate of the reactant [1-3]. Internal mass transfer that describes the transport of the reactants from the catalyst pore mouth to the actives sites inside the pores can influence the product selectivity in case it is slower than the desired chemical reaction on the catalyst surface via secondary reactions [1, 3, 4].

Mass transfer effects in APR are scarcely described in literature. Few studies are reported though for APR of ethylene glycol or sorbitol [3-6]. For hydroxyacetone (HYDA) conversion only gas phase reforming has been investigated [7]. The influence of external mass transfer limitations were not observed in these studies, however, it is suggested that internal mass transfer can decrease hydrogen selectivity [3, 4], via alkane formation as discussed in earlier in this thesis.

External mass transfer depends on the feed flow rate, but also on the catalyst particles size. When a catalyst is subjected to the liquid feed (fluid) a boundary layer of this fluid is formed around the catalyst grain. If diffusion of the reactant is limited in the fluid, the time for it to diffuse through the boundary layer increases. This means that the conversion of the reactant is hindered. The boundary layer may get bigger as the grain size gets smaller given that the flow rate is not affected. Therefore, both feed flowrate and catalyst grain size can influence the external mass transfer. Means of probing this limitation is by introducing feed at different rates while catalyst mass versus feed flow ratio is kept constant.

Feed injection in APR is often discussed as a critical parameter in the design of a reactor and design of injection nozzle is suggested to be a key element in the design. Efficient mixing of the reactants is important aspect of limiting transport limitations. Homogeneous mixing should be obtained to avoid external mass transfer limitations [8].

Parameters that influence the internal transport of reactants inside the catalyst pores and to the active sites are catalyst grain size and temperature of the reaction. When catalyst pores get narrower the mean free path of the reactant
to diffuse through the pores to the active sites becomes shorter. Therefore, the smaller the grain size suitable for the reactant molecules to diffuse through, the faster the diffusion can be. The consequence of the slow diffusion through the pores gives more time for the reactant/intermediate/products to diffuse away from catalytic sites avoiding further secondary reactions which can cause decrease in the selectivity of the desired product.

Temperature also influences the rates of the reaction. In Figure 1 the rate constant is plotted with temperature for the kinetic (diffusion limitation free) and diffusional limitation regions. The plot is based on Arrhenius equation (Eq. 1).

\[ k = Ae^{-\frac{E_a}{RT}} \]  

(1)

At low temperatures the activation energy is not influenced by the diffusional limitations. At higher temperatures when rates increase naturally, but diffusion of the reactants are severely limited, the observed activation energy will become approximately half of the true value. Activation energy in APR conditions has been reported by Shabaker et al. [5] as 110 kJ/mol in 5 wt% ethylene glycol conversion over Pt/Al2O3 catalysts at 265 °C. Influence of temperature in the reaction chemistry is interesting also for other reasons. Higher temperature may influence the catalyst stability. Furthermore, conversion is increased and thermodynamically H2 is favored at higher temperatures [9]. However, typically higher conversions in APR lower the selectivity to H2 as side reactions increase [10].

Mass transfer effects can also be probed with a Madon-Boudart criterion [4, 11]. In this criterion the rate of the reaction is equal to the number of surface
sites in a regime free of transport limitations. This criterion will therefore probe both external and internal mass transfer effects. The challenge in using this criterion is to carefully prepare catalysts with similar dispersions.

In this chapter we study possible mass transfer limitations for the developed catalyst Pt/C for APR of HYDA. We study external mass transfer limitations by keeping space-time fixed (W/U). We prepared 2 catalysts with different grain size to probe also internal mass transfer effects as well as influence, if any, for the product selectivity. Furthermore, attempts were made to study influence of temperature on product selectivity and estimate activation energy. The latter will also give indication of kinetics versus diffusional effects.

2 Experimental

2.1 Catalyst preparation

Platinum was loaded over carbon support (Sibunit, Boreskov Institute of Catalysis) by applying wet impregnation technique in order to achieve a nominal Pt loading of 1.5 wt%. The supports were carbon in 2 different grain size: 100-250μm and 70-100 μm.

Wet impregnation was performed by immersing the support in the aqueous precursor solution (1.8 g water/g support). Dihydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆•6H₂O) with 37.5 wt% Pt loading was used as precursor salt (Alfa Aesar GmbH). After this, the mixture was heated in an oil bath at 100 °C under constant stirring (between 100-200 rpm) and by using a rotary evaporator, the excess water was removed under vacuum. The dried catalyst powders were reduced under N₂ and H₂ flows (each gas flow 100 ml/min) at 100 °C for 5 hours with the rate of 5 °C per minute and subsequently put under thermal treatment in N₂ (200 ml/min) 300 °C for 15 hours (5 °C/min).

2.2 Catalyst characterization

Physicochemical properties of catalysts were examined by X-ray fluorescence (XRF), Brunauer-Emmett-Teller (BET) surface area analysis, CO chemisorption and transmission electron microscopy (TEM).

2.3 Catalytic performance tests

Catalyst performance was tested with 2.5 wt % hydroxyacetone aqueous solution (95%, Alfa Aesar GmbH). Testing of catalysts were done by investigating external mass transfer effect by varying flow rate of the feed U while keeping the catalyst weight and feed flow ration constant (W/U). In these tests the flowrate was 1 ml/min and 2 ml/min, while catalyst weight was 0.5 g and 1 g respectively. Further, internal mass transfer was studied by using 1 ml/min feed flow rate and 0.5 g of catalyst at 3 different temperatures, 225 °C/35 bar, 250 °C/50bar and 275 136
°C/75 bar. After the highest temperature, the initial temperature of 225 °C/35 bar was resumed to test the stability of the catalysts after experimenting at higher temperatures. Carbon balance in the experiments were between 81-97%.

3 Results

3.1 Catalyst characterization

Catalyst properties were measured by BET adsorption isotherm, XRF, CO chemisorption and TEM imaging. The surface area of catalysts measured by BET are shown in Table 1. As can be seen the surface area of the catalysts are similar 334 - 350 m²/g. After APR the specific surface areas decreased slightly, maximum of 10%.

Pt loading of the catalysts are presented in Table 2. I-Pt/C and II-Pt/C have the weight metal loadings of 1.4 and 1.7 wt%, respectively. A slight decrease in metal loadings after APR was observed. However, the decrease in loading was less than 10% for both of the catalysts tested. Comparing to reaction conditions, reaction a-c affected metal loading in similar rate for both catalysts, declining to approximately 8-10% for I-Pt/C and 3-4% for II-Pt/C.

The Pt particle size and dispersion measured by CO chemisorption are given in Table 3. The values were obtained from CO chemisorption for all catalysts. I-Pt/C and II-Pt/C have the metal sizes of 2.6 and 3.2 nm, respectively. Reaction under APR resulted in agglomeration of Pt. For I-Pt/C the Pt size increased from 2.6 nm to 6.8 nm in reaction a and for b and c the increase was to 3.9 nm and 8.6 nm, respectively. For II-Pt/C the increase was more steady for reactions a-c from between 5.9-7.9 nm, respectively. The Pt dispersion changed in similar manner.

<table>
<thead>
<tr>
<th>Table 1. BET surface area of fresh and spent catalysts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>I-Pt/C</td>
</tr>
<tr>
<td>II-Pt/C</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction condition 225 °C/35 bar, W<sub>cat</sub>= 1 g, u=2 ml/min

<sup>b</sup> Reaction condition 225 °C/35 bar, W<sub>cat</sub>= 0.5 g, u=1 ml/min

<sup>c</sup> Reaction condition T=225-275 °C, p= 35-75 bar, W<sub>cat</sub>=0.5 g, u=1 ml/min
Table 2. Metal loading for the fresh catalysts and for the spent catalysts under the conditions studied.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh</th>
<th>Spent&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Spent&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Spent&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-Pt/C</td>
<td>1.4</td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>II-Pt/C</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
<td>1.7</td>
</tr>
</tbody>
</table>

a) Reaction condition 225°C/35 bar, W<sub>cat</sub>=1g, u=2ml/min  
b) Reaction condition 225°C/35 bar, W<sub>cat</sub>=0.5g, u=1ml/min  
c) Reaction condition T=225-275°C, p=35-75 bar, W<sub>cat</sub>=0.5g, u=1ml/min

Pt size was also estimated by TEM imaging and the results are shown in Figures 2 and 3. The difference in Pt size is clear between CO chemisorption and TEM measurements for the fresh catalysts. TEM imaging was performed for the spent catalysts only for the catalysts that underwent the reaction a. this shows that slight increase in Pt size was observed for all the catalysts.

Table 3. Pt particle size and dispersion measured by CO chemisorption for the fresh catalysts and for the spent ones for reactions a-c.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt particle Size</th>
<th>Dispersion</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Spent&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Spent&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Spent&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Fresh</td>
<td>Spent&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>nm</td>
<td></td>
<td></td>
<td></td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>I-Pt/C</td>
<td>2.6</td>
<td>6.8</td>
<td>3.9</td>
<td>8.6</td>
<td>45</td>
<td>17</td>
</tr>
<tr>
<td>II-Pt/C</td>
<td>3.2</td>
<td>5.9</td>
<td>7.9</td>
<td>7.2</td>
<td>36</td>
<td>19</td>
</tr>
</tbody>
</table>

a) Reaction condition 225°C/35 bar, W<sub>cat</sub>=1g, u=2ml/min  
b) Reaction condition 225°C/35 bar, W<sub>cat</sub>=0.5g, u=1ml/min  
c) Reaction condition T=225-275°C, p=35-75 bar, W<sub>cat</sub>=0.5g, u=1ml/min

138
Figure 2. TEM Images of Fresh (a) & Spent (b) catalyst and particle size distribution (c) for Pt/C (100μm – 250 μm). These images are recorded from the catalyst used in APR of HYDA at 225 °C/35bar, with 2ml/min flow rate and 1 g of catalyst.
Figure 3. TEM Images of Fresh (a) & Spent (b) catalyst and particle size distribution (c) for II-Pt/C (70-100 μm). These images are recorded from the catalyst used in APR of HYDA at 225 °C/35 bar, with 2 ml/min flow rate and 1 g of catalyst.

3.2 Catalysts performance

For this study experiments were performed to identify the effect of three parameters; fluid velocity, grain size, and temperature on the catalyst performances. They were examined to determine possible mass transfer limitations: especially the effect of flow rate of the feed for external mass transfer limitation, and the grain size for the internal mass transfer limitation. Effect of temperature was studied by increasing it from 225 °C to 250 °C and 275 °C. In Figure 4 the change in the conversion levels are shown for I-Pt/C. As can be seen high conversions are obtained already at 250 °C and at 275 °C complete conversion was obtained. Therefore, we did not consider results at 275 °C and did not calculate activation energy as we only had 2 valid measuring points. However, results from higher temperature can be used for information of product selectivity and catalyst stability.

140
3.2.1 Stability

Catalyst stability was investigated at different temperatures (225–275 °C). Total Conversion at these temperatures for I-Pt/C (100-250 µm) and II-Pt/C (70-100 µm) catalysts is presented in Figure 5. To see if the temperature and time on stream influenced catalyst performance, after 275 °C, the temperature was decreased back to 225 °C. Catalyst II-Pt/C showed the higher Total Conversion (70%) at 225 °C whereas I-Pt/C had initial total conversion of 65%. Increase in
temperature increase Total Conversion for both catalysts, at 250 °C 96% and 100% conversion were reached for I-Pt/C and II-Pt/C, respectively. As almost full conversion was reached at 250 °C, testing catalysts with this feed composition at 275 °C did not change the Total Conversion and therefore, this temperature was not taken into the consideration in the further studies for this chapter. After 275 °C the temperature was decreased back to 225 °C where the initial conversion levels were restored to confirm that the catalyst were stable during the period of the catalyst testing with respect to temperature and time on stream.

3.2.2 External diffusion effects

External diffusion effect were studied while keeping space-time ($W/F_{HYDA}$) similar for both catalysts. The experiments were carried out under 1 ml/min and 2 ml/min flowrates at 225 °C and 35 bar by using 2.5% HYDA solution. In Figure 6 Total Conversion is shown for both catalysts under these conditions. For II-Pt/C slight difference is observed as the Total Conversion at 2 ml/min was slightly lower (65%). For I-Pt/C the conversion levels were the same 54%.

The performance was compared also in terms of HYDA carbon conversion rate shown in Table 4. This means that the rate is per converted HYDA carbon. The Total conversion of HYDA carbon at 1 ml/min was 0.84 mmol/min*m$^2_{Pt}$ and with 2 ml/min 0.75 mmol/min*m$^2_{Pt}$ for I-Pt/C. Carbon to Gas conversion rates for this catalysts were fairly similar 0.67-0.70 mmol/min*m$^2_{Pt}$. For II-Pt/C the rates were higher 0.84-0.9 mmol/min*m$^2_{Pt}$ but the trends similar.

![Figure 6. Total Conversion of HYDA under different flowrates in APR over I-Pt/C (100-25 μm) and II-Pt/C (70-100 μm) catalyst at 225 °C/35 bar. Catalyst loadings 0.5 g for 1 ml/min flowrate and 1 g for 2 ml/min flowrate.](image)
Table 4. Rate of carbon conversions per available Pt surface area during external mass transfer study of I-Pt/C (100-250 μm) and II-Pt/C (70-100 μm) at 225 °C/35 bar.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Feed flow rate</th>
<th>Conversion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ml/min</td>
<td>Total mmol/min* m² Pt</td>
</tr>
<tr>
<td>I-Pt/C</td>
<td>1</td>
<td>0.84</td>
</tr>
<tr>
<td>I-Pt/C</td>
<td>2</td>
<td>0.75</td>
</tr>
<tr>
<td>II-Pt/C</td>
<td>1</td>
<td>0.90</td>
</tr>
<tr>
<td>II-Pt/C</td>
<td>2</td>
<td>0.84</td>
</tr>
</tbody>
</table>

3.3 Internal diffusion effects

The effect of grain size to catalyst performance was studied with I-Pt/C (100-250 μm) and II-Pt/C (70-100 μm) at 225 °C/35 bar by using 1 g catalyst and 2 ml/min of 2.5% HYDA solution. In Figure 7 the Total Conversion of HYDA and the Carbon to Gas conversion are presented. As can be seen, the conversions increase in the order of II-Pt/C > I-Pt/C.

Gaseous phase composed mainly of H₂, CO, CO₂ and CH₄ (Figure 8) with a small amount of ethane detected. The catalysts showed similar gaseous products selectivity.

Figure 7. The Total HYDA conversion and Carbon to Gas conversion I-Pt/C (100-250 μm) and II-Pt/C (70-100 μm) catalysts.
The liquid phase composed mainly of acids, alcohols, diols and aldehydes. The results are shown in Figure 9 and liquid products are grouped based on components. Major products were acetic acid, ethanol, 2-propanol and 1,2-propanediol (1,2-PDO). The results show some differences for the catalysts, main in the formation of alcohols. I-Pt/C catalyst showed higher selectivity (approximately 6 %) compared to II-Pt/C (approx. 4%).

Figure 8. Gas phase composition during APR of 2.5 wt% HYDA at 225 °C/35 bar , 2ml/min flowrate, 1 gram of catalyst.

Figure 9. Gas phase composition during APR of 2.5 wt% HYDA at 225 °C/35 bar , 2ml/min flowrate, 1 gram of catalyst.
3.3.1 Effect of temperature on product selectivity

The effect of temperature for product selectivity was studied at 2 different temperatures (225 °C and 250 °C), and by applying system pressure 35 and 55 bar, respectively.

In Table 5 the carbon conversion rates with the corresponding conversion levels are shown for both catalysts at the temperatures studied. As could be expected the rates and conversion levels increased with the increase in temperature. For both catalysts similar total carbon conversion rates were observed 0.90-0.96 mmol/min*m²Pt at 225 °C and at 250 °C 1.29 mmol/min*m²Pt. Carbon to gas conversion showed slightly higher differences approximately 13% higher rate for II-Pt/C than I-Pt/C.

Selectivity to gas phase products and liquid phase products are shown separately for the catalysts. In Figure 10 the selectivites are shown for I-Pt/C at the two temperatures. Interestingly, as the conversion increases the H₂ selectivity increases as well. Along with increased hydrogen selectivity, CO₂ selectivity improves with the expense of CO selectivity indicating an improved WGS. Methane selectivity increases slightly, but not as dramatically as the others with the temperature. This indicates that route to methane is independent of the CO and CO₂ routes and is not result of a methanation of CO₂-species.

Table 5. Conversion rates of I-Pt/C and II-Pt/C catalysts at the studied temperatures. Reaction conditions W= 0.5 g and u = 1 ml/min.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature</th>
<th>Conversion Rate</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td></td>
<td>Total</td>
<td>Carbon to Gas</td>
</tr>
<tr>
<td>I-Pt/C</td>
<td>225</td>
<td>0.90</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>I-Pt/C</td>
<td>250</td>
<td>1.29</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>I-Pt/C</td>
<td>*225</td>
<td>0.90</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>II-Pt/C</td>
<td>225</td>
<td>0.96</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>II-Pt/C</td>
<td>250</td>
<td>1.29</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>II-Pt/C</td>
<td>*225</td>
<td>0.90</td>
<td>0.84</td>
<td></td>
</tr>
</tbody>
</table>
Figure 10. Gas phase selectivity over I-Pt/C catalyst (100-250 μm) at 225 °C and 250 °C during HYDA APR (0.5 g catalyst, flowrate 1 ml/min).

Liquid phase product selectivities (right hand side Figure 10) also showed changes when increasing the temperature from 225 °C to 250 °C. Selectivity to liquid products, expect for acids and alcohols remain similar with temperature, but diols, mainly (1,2-PDO) decreases with temperature.

In Figure 11 on the left hand side the selectivities to gas phase products and liquid phase products over the II-Pt/C catalyst are shown. As the temperature was increased to 250 °C, H₂ and CO₂ selectivity increased, while the CO selectivity decreased. Moreover, slight increase was observed in the CH₄ selectivity. Thus, the trends between I-Pt/C and II-Pt/C for gas phase products are similar.

Liquid products selectivity is shown in the right hand side of Figure 11. Similar behaviour was observed as with the II-Pt/C catalyst. Alcohols and acids were not significantly influenced by temperature, but diol/triol formation decreased with increase in temperature to 250 °C.

Figure 11. On the left hand side Gas phase selectivities and on the right hand side Liquid phase selectivities over II-Pt/C catalyst (70-100 μm) at 225 °C and 250 °C (0.5 g catalyst, 1 ml/min flowrate).

146
4 Discussion

4.1 Catalyst properties and the effects of reactions conditions thereof

The surface areas of fresh catalysts were similar for II-Pt/C (350 m$^2$/g) and III-Pt/C (334 m$^2$/g). Furthermore, pore volume distribution graphs of fresh catalysts in Supplementary Information (Figures S1-S4) shows that I-Pt/C and II-Pt/C have similar porosity.

The surface areas of the catalysts decreased slightly after the APR reactions, as can been seen in Table 1. By comparing the pore area distribution plots of fresh catalysts with those of spent ones in Supplementary Information, it is clear that some of the smaller mesopores were lost. The reason can be speculated, can be due to blockage by coke or due to changes in support structure due to APR conditions. However, the observed decrease in surface area is small (2-11%) and not expected to affect the observed catalysts performance significantly.

The XRF measurement showed some differences for the loading of the fresh catalysts. Due to this reason, the rates were calculated based on the surface area of the catalyst to compare the performance more accurately. Post-mortem analysis showed that some Pt was lost during APR. For reaction $a$ I-Pt/C and II-Pt/C in reactions $a$-$c$ the loss was 7-14% and 0-6%, respectively. Looking at the loss in activity, it is the same order of magnitude, 9-10% from initial which indicates that the loss of Pt correlates as least partly with the loss of metal.

CO chemisorption and TEM imaging results were presented in Tables 3, and Figures 2 and 3. For the fresh catalysts, the Pt size and dispersion measured by chemisorption varied between 2.6 nm and 3.7 nm. The chemisorption data for the spent catalysts, showed sintering of Pt based on both catalysts. Relatively CO chemisorption showed higher decree of Pt agglomeration than TEM. The reason for this may be due to the fact that CO chemisorption measured the available surface area based on CO adsorption and TEM all visible Pt particles in the micrographs. During the TEM imaging some difficulties were faced in measuring the Pt size as Pt particles were not visible in all images as the particles tend to melt in the background. This has been reported earlier [10].

For reaction $b$ and $c$, Pt agglomeration occurred as well (Table 4). However, the observed increase in Pt size was similar to what observed in reaction $a$, thus the conditions used in reaction $b$ and $c$ seemed not to enhance the increase in Pt size further.
4.2 Mass transfer effects and product selectivity

In the previous chapters we have shown that Pt/C is stable catalysts in APR of small oxygenates. In this chapter we measured the stability of the catalyst under 3 temperatures between 225 °C-275 °C. The results showed that the performance of the catalyst was not compromised as the initial performance was resumed after decreasing the temperature back to 225°C. High conversion (96%) was already obtained at 250 °C and at 275 100%, therefore we did not consider results from the experiments at 275 °C. One way to overcome this and operate at lower conversion levels would have been to increase the concentration of the feed or increase the flowrate of the feed. However, due to operational reasons it was not possible to increase the flowrate as stabilizing the temperature for the system became more challenging. Further, initial tests with HYDA reforming at higher feed concentration showed increase of thermal liquid phase conversion and therefore, lower feed concentration was used throughout this thesis. Two temperature points are not enough to calculate activation energy properly and was not attempted. However, the experiments at the two temperatures provided information on the product selectivity discussed later in this section.

The effect of feed flow rate was studied to estimate possible external mass transfer effects during APR of HYDA. The results shown in Figure 6 confirm that external limitations are not present as the conversion levels remain similar when flowrate is changed from 2 ml/min to 1 ml/min while keeping space-time constant. Also, the conversion rates were similar under these conditions (Table 4 and 5). Furthermore, we calculated Carberry numbers (Ca) for both catalysts and the results are shown in Table 6. As can be seen the calculated values are well below the target values (2.4 x 10^1 < 0.15). Having this criterion fulfilled, we can conclude that the external mass transfer is not playing a role in APR of HYDA under these conditions.

Internal mass transfer limitations in APR have been reported to affect H2 selectivity [3, 4]. When the transfer of H2 from the catalyst pores to the gas phase is slower than the rate of reaction, possibility for H2 being consumed by hydrogenation reactions increase [3]. This can lead to increased alkane selectivity or increased selectivity of liquid phase hydrogenation products, such as 1,2-PDO and alcohols.

Comparing the selectivities for gas phase products under the two flowrates for I-Pt/C catalyst very similar results for both gas phase and liquid phase products were observed. For II-Pt/C the results showed some differences, however, the overall trends were the same. Furthermore, comparing the selectivities for the I-Pt/C and II-Pt/C with each other, the trends are the same and no large differences are visible. This also suggests that under these conditions the product selectivities during APR of HYDA are not sensitive to small differences in conversion level (Table 4 and 5).
Table 6. Transport criteria for the 2 catalysts calculated. Conditions used were 225 °C/35 bar, 1ml/min flow rate 0.5 g catalyst. The widest catalyst particle diameter was used for the calculations. First order reaction was assumed.

<table>
<thead>
<tr>
<th>Transport criteria</th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>I-Pt/C</td>
<td>II-Pt/C</td>
</tr>
<tr>
<td>Particle diameter, μm</td>
<td>100-250</td>
<td>70-100</td>
</tr>
<tr>
<td>Sites, μmol/g</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Target</td>
<td>Criterion</td>
</tr>
<tr>
<td>Ca</td>
<td>$2.4 \times 10^3$</td>
<td>$4.2 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{r_{v,p}^0 d_p^2}{a^7 k_c C_b}$</td>
<td></td>
</tr>
<tr>
<td>$C_{\text{WP}}$</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>$\frac{r_{v,p}^0 d_p^2}{C_s D_e}$</td>
<td></td>
</tr>
<tr>
<td>Length of axial dispersion</td>
<td>4.2</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>$\frac{L}{d_p} &gt; \frac{20 n}{Pe_a} \ln \frac{C_0}{C_f}$</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2$-TOF (min$^{-1}$)</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Madon-Boudart</td>
<td></td>
</tr>
</tbody>
</table>

Weisz-Prater criterion ($C_{\text{WP}}$) can be to estimate the effects of internal mass transfer. However, using this criterion requires knowledge of the reaction order. However, it can still be used to give an indication of these limitations. In Table 7 we show the calculated values for the studied reaction assuming first order reaction. Typically, if calculated $C_{\text{WP}}$ is well below 1, then internal diffusion limitations can be neglected and close to 1 or above they are most likely present. Our values are well below 1 (0.04). Furthermore, studies in APR are commonly performed with mesoporous materials [4, 12]. Mesoporous materials have a pore volume suitable for catalysis and usually free from mass transfer effects with smaller molecules as their diffusion in the catalyst pores is free from structural limitations. We used mesoporous carbon Sibunit for the studies performed in this thesis and with the criteria (Ca, $C_{\text{WP}}$) fulfilled as well as the similar $\text{H}_2$ selectivity at 225 °C indicates that internal diffusion is not a major issue in our study.
Shabaker et al. [4] studied APR of EG at 210 °C and 225 °C by applying Madon-Boudart criterion. This criterion assumes that the rate of the reaction is proportional to the number of active sites on the catalyst per unit volume of the reactor in absence of any transport limitations. Thus, by preparing catalysts with different loading on the same support, this criteria probes both external and internal transport limitations without changing the flowrate of the reactants. However, the challenge of using this criteria lies in catalyst preparation and pretreatment, as one has to obtain similar geometry and dispersion of sites while altering the loading of the catalyst. Shabaker et al. [4] presented the catalyst performance in terms of H₂-TOF and observed that for a Pt/Al₂O₃ catalyst with a higher Pt loading (3.4 wt%, grain size 63-125 μm) some transport limitations were present and these were lowering the H₂-TOF. We calculated the number of sites on the catalysts and this was found to be the same for both catalysts (31 μmol/g). It is not a surprising as the catalysts are prepared with the same carbon only with different grain size and the BET surface area are very similar. Looking at the H₂-TOF for these catalysts, a difference can be seen. For I-Pt/C (100-250μm) H₂-TOF of 18 min⁻¹ was obtained whereas for II-Pt/C (70-100μm) H₂-TOF of 23 min⁻¹ was achieved. Based on Madon-Boudart criterion transport limitations are therefore present. H₂-TOF for both catalysts at higher feed flowrate (2 ml/min, 1 g catalyst) was the same. Furthermore, based on the previous discussed data and calculation of the Carberry number, a possible limitation is in internal diffusion rate of H₂. Neira D’Angelo et al.[3] studied sorbitol APR comparing a microchannel reactor to a fixed bed reactor. They observed that mass transfer was not an issue for sorbitol conversion, but for consumption of H₂ by fast side reactions as H₂ transport from the catalyst sites to gas phase is limiting. In our case the differences in selectivity and rates are small. To know for sure of the effect, a catalyst with even smaller grain size should have been tested in the comparison. However, this could have led to a pressure drop in the reactor. In addition, Madon-Boudart criterion is dependent on the fact that the sites should be similar in number, but also in size and geometry. Without careful investigation of these, it is possible that deviation can be present and affecting the comparison. If the limitations had been present, it cannot be concluded with the gathered information.

Attempts to calculate activation energy were not successful as high conversion were achieved already at 250 °C. This would have given more information about transfer limitations as the they become more sever at higher temperatures (Figure 1). However, experiments at higher temperatures can provide information about the product selectivities. In Figures 10 and 11 selectivities for I-Pt/C and II-Pt/C are shown. The most significant change in the product selectivities was the increase of H₂ at higher temperature. As discussed in previous chapters the levels of CO were high in our studies indicating insufficient WGS. The equilibrium constant of WGS is only slightly less at 250 °C.
\( K_{\text{WGS}} = 2968 \) than at 225 °C (\( K_{\text{WGS}} = 3147 \)) when liquid water is reactant in the reaction (Eq. 2).

\[
\text{CO (g) + H}_2\text{O(l) } \leftrightarrow \text{H}_2\text{(g) + CO}_2 \quad \text{\( K_{\text{WGS}} = 3147 \text{ bar} \) (2)}
\]

However, the equilibrium constant for HYDA reforming increases significantly between these temperatures. Therefore, the increase of \( \text{H}_2 \) at higher temperature seems to be due to the driving force of the increased \( \text{CO} \) produced from the HYDA reforming. Interestingly, the increase in conversion did not increase the selectivity to side products that are reported to occur when conversion levels increase. Interestingly, methane selectivity increased only 15-20% whereas the increase in hydrogen selectivity was approximately 50%. Methane can form in these conditions via several routes, by incomplete reforming of HYDA or via methanation (Eq 3).

\[
\text{CO (g) + 3H}_2\text{(g) } \leftrightarrow \text{CH}_4\text{(g) + H}_2\text{O (l)} \quad \text{\( K_{\text{CH4}} = 6.1x10^8 \) (3)}
\]

Equilibrium towards methanation decreases when temperature is increased, which is in line with our results. However, all the liquid products formed at 225 °C can result in methane formation when they are reformed further. As we presented in Chapter 5 in Scheme 1 via routes 1a and 2 methane can be a by-product of ethanol and methanol formation in APR of HYDA. At 225 °C both methanol and ethanol are observed in the liquid product stream, but at 250 °C the formation of these products decreases for both catalysts. This could be one of the reasons why methane formation does not increase as these routes become less dominating. However, while formation of these alcohols reduces significantly with the increase in temperature, the formation of 2-propanol increases a lot compared to selectivity at 225 °C. This indicates that dehydration/hydrogenation route from HYDA increased. However, the changes in the selectivities in the liquid phase products are rather small compared to gas phase products.

To summarize, Pt/C is a stable and active catalyst for APR of HYDA even at higher operating temperatures. Our results and the calculated criterion under the conditions studied exclude the effect of external mass transfer limitations. Studying the internal mass transfer effects showed that in the range of support particle size and calculation of criteria for the transfer limitations, the results are not completely unambiguous. Based on selectivities and calculated \( \text{GWP} \) indicated that internal mass transfer limitations did not affect the observed product distributions.
5 Conclusions

Aqueous phase reforming of HYDA was studied under different conditions to estimate roles of mass transfer. The results combined with calculations of transport criteria showed with good range that the rate of HYDA APR was not influenced by them.

Influence of temperature to product selectivity was studied. It showed that hydrogen selectivity can be increased over Pt/C catalyst by increasing the temperature of the reaction. This resulted in improved WGS and lowered CO selectivity.

Pt/C excellent catalyst for APR of small molecules as shown in Chapter 4, 5 and 6. It is stable under the reaction conditions against structural changes and carbon deposits. Using mesoporous carbon at smallest possible grain size should be used for minimizing internal transport issues especially when larger molecules are considered. Furthermore, considering the mesoporosity of Sibunit, its low cost, efficient functioning of the Pt/C, its stability and excellent performance, and easy possibility of the Pt recovery after use makes Pt/C this an excellent choice and gives lots of promise for APR application.

6 References


153
Figure S1. Pore area and pore diameter for the fresh I-Pt/C catalyst.

Figure S2. Pore area and pore diameter for the spent I-Pt/C catalyst (reaction a).
Figure S 3. Pore area and pore diameter for the fresh II-Pt/C catalyst.

Figure S 4. Pore area and pore diameter for the spent II-Pt/C catalyst (reaction a).
Chapter 8

Conclusions and further suggestions

The work in this thesis is concluded in this chapter. In the first part, the findings of each chapter are summarized together. The second part discusses the future remarks possibilities and challenges based on the findings of this thesis.
Chapter 8

1 Conclusions

Aqueous phase reforming is an interesting process for producing hydrogen from diluted biomass based aqueous waste streams. Complex nature of biomass feedstocks is a challenge for the commercialization of this process. Especially, design of a stable and efficient catalyst to maximize hydrogen yields is needed.

In this thesis, current status and future challenges of APR was presented in Chapter 2. Catalyst design for APR needs to take into consideration stability of the catalyst to avoid deactivation on stream. Under the higher temperatures and pressures used stability of catalytic materials can suffer from several drawbacks. Examples are sintering and leaching of the support material or sintering of the active metal. Further, high carbon to gas conversions are desirable to ensure full gasification of the feed and iii) avoiding formation of liquid by-products that are subjectable to form coke on the catalyst and result in blockage of the active sites or even catalyst pores. Finally, selectivity to hydrogen should be maximized by enhanced WGS reaction and by avoiding reactions that result in C-O-bond cleavage as these lead in gas phase to formation of methane and other gas phase alkanes lowering H₂ yields. Chapter 3 details the experimental techniques used in the study.

In Chapter 4 the performance of Pt/γ-Al₂O₃ in APR of EG was studied and compared to Pt/AlO(OH), the hydrated form of γ-Al₂O₃. Formation of Boehmite phase was monitored under ATR-IR spectroscopy and the difference of OH-groups between γ-Al₂O₃ and AlO(OH) was studied. The Pt/γ-Al₂O₃ catalyst, was initially active, deactivated time on stream whereas Pt/AlO(OH) remained stable. Remarkably, the selectivity to hydrogen was higher with Pt/AlO(OH). We conclude this to be due to its higher concentration of OH-groups on the support that enhances bi-functional reforming mechanism involving carbonaceous species on Pt and water activation via the hydroxyl groups formation on the support as well as enhancing oxidation of Pt. Boehmite supported catalyst is a stable and active for H₂ production from small biomass molecules, such as ethylene glycol.

However, as shown in Chapter 5, oxide supported catalysts such as Pt/AIO(OH) and Pt/ZrO₂ suffer from deactivation when reforming more functionalized biomass feeds, such as hydroxyacetone. The acidity of the support material causes condensation reactions on the support surface that leads to carbon deposits on the catalyst. Therefore, a less acidic material, such as mesoporous carbon is more suitable for APR of complex feedstocks. Pt/C was found to be stable and active for APR of HYDA. The catalyst performance needs further improved by increasing WGS activity to convert CO to CO₂ more efficiently.

Catalyst performance can be tailored in many ways and it has been indicated that the Pt size may influence a catalyst’s performance in APR. In Chapter 6 Pt size and distribution was varied over the carbon supported Pt catalysts. The results showed that
a more egg-shell type distribution of Pt and larger Pt particles had an advantage in APR of ethylene glycol. Furthermore, larger Pt particles appeared to be more active in C-C cleavage and improve hydrogen production rate (H₂-TOF).

Lastly, in Chapter 7 the possibility of diffusional effects in APR of hydroxyacetone was studied along the influence of temperature on product distribution. Effect of external diffusion limitations were excluded in our conditions, however the presence of internal diffusion limitations could not be ruled out entirely. However, calculated transport criteria and the product selectivities showed small probability for their existence. Increasing temperature in APR of HYDA improved hydrogen selectivity by enhanced WGS. Mesoporous carbon is an excellent choice for APR due its low cost, efficient functioning of the Pt/C, its stability and excellent performance, and easy possibility of the Pt recovery after use makes Pt/C this an excellent choice and gives lots of promise for APR application.

2 Remarks for future research based on the findings in this thesis

APR is challenging process that requires a stable and selective catalyst for maximized hydrogen production. In this thesis Pt/C catalyst was found to be a suitable candidate for this purpose due to its stability and activity under theses challenging conditions. However, the WGS activity of this catalyst should be enhanced. Therefore for the future suggestions, it proposed to study the mechanism of WGS under APR conditions. In steam reforming the water is known to be activated on the support by its OH-groups. However, so far there is no evidence how this reaction undergoes over carbon supported catalysts. In addition to this, hydrogen selectivity with Pt catalysts has been improved by adding Ni on Pt/γ-Al₂O₃ catalyst. Therefore, it would be interesting to study whether the same improvement could be achieved with carbon supported Pt catalysts.

Furthermore, HYDA is an interesting model compound as it represents ketone fraction of the biomass feeds. Reforming of HYDA leads to methane formation (appr. 20 mol%). Based on the results this is due to inefficient reforming of HYDA, rather than methanation on the catalyst. Studying the reaction mechanisms of the HYDA APR would help to understand how this pathway could be prevented and hydrogen selectivity further improved.
Acknowledgements

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With love and respect,

Kaisa.
Scientific contributions

Chapter 2


Chapter 4


Chapter 5


Chapter 6


Chapter 7


Conference proceedings


Anna Kaisa Kristiina (Kaisa) Vikla was born on 1\textsuperscript{st} September 1982 in Nurmijärvi, Finland. She studied chemistry at University of Helsinki and received Bachelor of Science degree in 2008. After working in paint and coatings industry for 2 years, she started studies in Aalto University. In 2012 she graduated with a Master’s degree in Chemical Engineering from Industrial Chemistry group.

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